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## Application of the newly developed 3D transport code $r^3t$ to selected field cases

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### **Abstract:**

To model the transport of contaminants in connexion with long-term safety analyses of repositories for radioactive waste recently the numerical model  $r^3t$  was developed. In the following first applications of  $r^3t$  are presented. The results of modellings of the transport of zinc at the sewage treatment facility in Cape Cod, Massachusetts, and of trace elements in the frame work of the in-situ diffusion experiments DI-A and DR at the underground laboratory Mont Terri are shown.

## **1 INTRODUCTION**

For long-term safety analyses of final repositories and landfills of hazardous wastes in deep geological formations the potential release of pollutants is assessed for relevant scenarios. To perform such analyses for large, three-dimensional, and hydrogeologically complex areas the two program packages  $d^3f$  (distributed density-driven flow) [ 3 ] and  $r^3t$  (radionuclides, reaction, retention, and transport) [ 4 ] to model flow and transport were recently developed lead-managed by GRS. These computer codes enable the modelling of density-driven flow like it occurs in the vicinity of salt domes and the transport of pollutants taking the relevant interactions for long-term safety analyses.

## **2 THE TRANSPORT CODE $r^3t$**

The numerical model  $d^3f$  was developed from 1994 to 1998 while  $r^3t$  was generated from 1998 until 2003. Six and four working groups, respectively, of German or international universities were involved in the development lead-managed by GRS. Both of the codes use Finite-Volume discretisation and unstructured grids to enhance the resolution of hydrogeological heterogeneities. Adaption techniques controlled by a-posteriori error estimators are applied to the grid and the time steps to ensure the optimal length in time and space. As the most effective solvers for large and sparse systems of equations multigrid algorithms are taken. Additionally the entire codes are parallelised so that they can be run on workstations, PCs, cluster of PCs, and massively parallel computers, too.

The overall objective of the  $r^3t$  project was the development of a computer code to simulate pollutant transport which meets the following demands: simulation of three-dimensional transport through porous or equivalently porous media, treatment of spacious and heterogeneous areas, consideration of advection, diffusion, and dispersion and interaction processes which are relevant to long-term safety analysis, applicability for radionuclide migration as well as for chemotoxic pollutants.

Often single processes are not independent but coupled. Transport of pollutants is often governed by other matters, which are migrating, too. These matters are natural (e.g. humic material) or artificial substances (e.g. EDTA). In the following they are called complexing agents. To consider the impact of complexing agents, transport of complexing agents is modelled, too. The sorption and solubility parameters are taken into account by functions depending on the concentrations of complexing agents ("smart  $K_d$ "). Since the concentration of the complexing agents are space and time dependent, sorption and solubility parameters themselves become space and time dependent.

In addition, for radionuclides the decay is considered within decay chains. Hence transport simulations of various radionuclides cannot be independently performed, since isotopes affect each other.

The individual interaction processes which affect the pollutants transport are given in the following: equilibrium and kinetically controlled sorption, both linear (Henry) and nonlinear (Langmuir, Freundlich), respectively; precipitation and diffusion into immobile porewater; complexation; colloidal transport and matrix diffusion via effective parameters. Later on the code was completed by anisotropical, element-specific diffusion and by element-specific porosity. At the beginning there was no intention to couple transport and geochemistry, but meanwhile the coupling of  $r^3t$  and the geochemical code Phreeqc [ 8 ] is in progress.

During transport modelling one makes use of the stationary or transient results of  $d^3f$  simulations: i. e. the Darcy velocity and the fluid density serve as input for  $r^3t$ .

### 3 APPLICATIONS

During developmental period the codes were subject to comprehensive tests by comparison to analytical and numerical solutions. To qualify the codes additional tests were performed. In the following two of these tests are described.

#### 3.1 Sewage treatment facility at Cape Cod, Massachusetts

The field site considered here is located in western Cape Cod, Massachusetts. About 59 years of land disposal of sewage effluent resulted in contamination of the aquifer with zinc (Zn). The sewage plant was opened in 1936 and shut down in 1995. Extensive measurement campaigns and field-tests were undertaken during the last years of operation and for the first years after closure.

The aquifer consists of medium to coarse sands and gravels [ 6 ]. The water table slopes to the south at  $\sim 1.6$  m per 1000 m. Groundwater flow direction is thus generally from north to south. The flow is nearly horizontal except for the areal recharge that results in a vertical flow component close to the water table. The water table altitude fluctuates about 0.80 m and the flow direction varies about  $16^\circ$  (c.f. Fig. 1) [ 7 ].

Downgradient from the disposal beds there was a zone of uncontaminated groundwater above the Zn-contaminated region. At 90 m downgradient a sharp transition in the thickness of the zinc plume was observed. Further downgradient the plume covered only the topmost 2-4 m of the contaminated region. The leading edge of the Zn-plume was sharp and was located approximately 400 m downgradient. In contrast, conservative, non-reactive constituents of the sewage plume formed a diffuse leading edge greater than 5500 m downgradient of the source.

Seasonal variations in the water table and the flow direction are small enough to allow an approximation of the true flow conditions as a steady-state flow. Thus, only the permeability and the boundary conditions are required to describe the flow field. The horizontal dispersion appears to be sufficiently small to reduce the spatial domain to a two-dimensional vertical cross-section without losing too much accuracy. The top boundary is supposed to be identical with the water table. Water from precipitation enters the aquifer here. The bottom

boundary is assumed to be a no-flow boundary. From the left hand side the contaminated water enters the domain horizontally thus assuming that the effluent from the disposal beds is outside the domain already completely mixed with the pristine groundwater. At the right hand side boundary the water leaves the domain (c.f. Fig. 2).

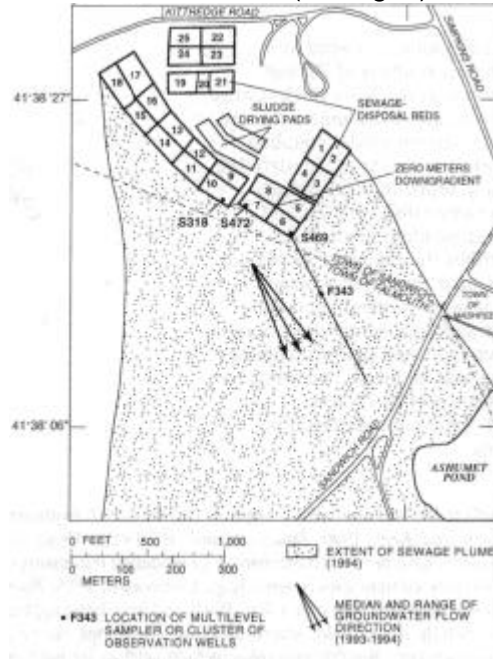


Fig. 1 Location of the area of sewage-contaminated groundwaters, facility layout and hydraulic gradient direction; from [ 7 ].

In all modelling efforts zinc has been fed to the modelled domain by using a constant Dirichlet boundary condition at the left hand side boundary. Variations of this value with time were not considered. In the present model a value of  $2 \mu\text{M}$  is applied for 59 years of model time. Afterwards this value is set to zero assuming instantaneous cessation of contamination.

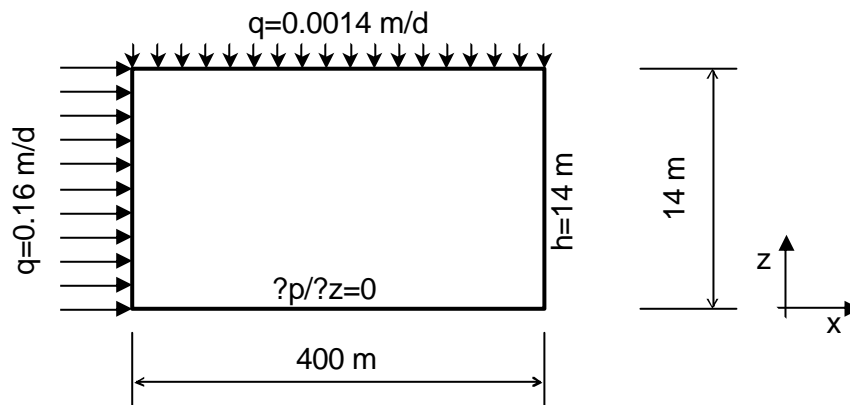


Fig. 2 Conceptual flow model.

Pristine groundwater and water coming from the surface have a pH of about 5.65. The pH-value of the groundwater downstream of the sewage plant is influenced by the effluents and changes with depth. Neither the pH-values nor the equivalent proton concentrations<sup>1</sup> of the water entering the domain over the left hand side boundary are given directly in the literature. The only hints can be found in figures showing the simulated pH-values like in [ 5 ].

<sup>1</sup> The pH-value is defined as the negative common logarithm of the proton concentration in [M].

In the present model the proton concentration is used as a primary variable for the modelling instead of pH-values because the pH-value is not an extensive quantity. The protons are assumed to be transported like a tracer, being subject to dispersion but not to retardation, i.e. buffering of pH by the sediment is neglected. After a model time of 59 years the equivalent to a pH-value of 5.65 is applied uniformly along the left hand side boundary.

The reason for the retardation of the zinc is sorption onto the surface of the sediment. Equilibrium adsorption can safely be assumed for the flow conditions at Cape Cod [ 5 ]. In combination with the fact that the amount of zinc adsorbed on the sediments amounts to less than one tenth of the saturation value, the adsorption process appears to be well described by the  $K_d$ -concept.

It is generally agreed that the sorption of zinc is proportional to the pH-value of the groundwater<sup>2</sup>. A correlation between the pH-value and a referring  $K_d$ -value can be derived from an adsorption isotherm which relates the concentration of adsorbed zinc to the pH-value. Sorption experiments with zinc and sediment material from Cape Cod were described by chemical models in order to predict these adsorption isotherms on a theoretical basis [ 1 ]. The functions presented in Fig. 3 are the result of a complex chemical model not yet implemented in  $r^3t$ , so an analytical function has to be found yet. For the task at hand it is necessary to cover only the range of pH-values between 5.5 and 6.5. A third order polynom is therefore fitted to this part of the isotherm for  $M/V = 400 \text{ kg/m}^3$ . The quality of this approximation to the isotherm can be judged from Fig. 3. The resulting  $K_d$ -function for the distribution coefficient is given in Fig. 3, too.

The development of the zinc plume and the pH-distributions until closure of the sewage plant after 59 years of operation is illustrated in Fig. 5 and Fig. 6. In contrast to proton transport the migration of zinc is impeded by sorption. Steady-state conditions with respect to proton transport arise after about 3 years while the zinc plume doesn't even reach the right hand side of the modelled domain after 59 years. Transport of zinc is much slower than the changes in the pH-values, so that the zinc always travels in a steady-state pH-milieu. Note the differing vertical and horizontal scale in the figures.

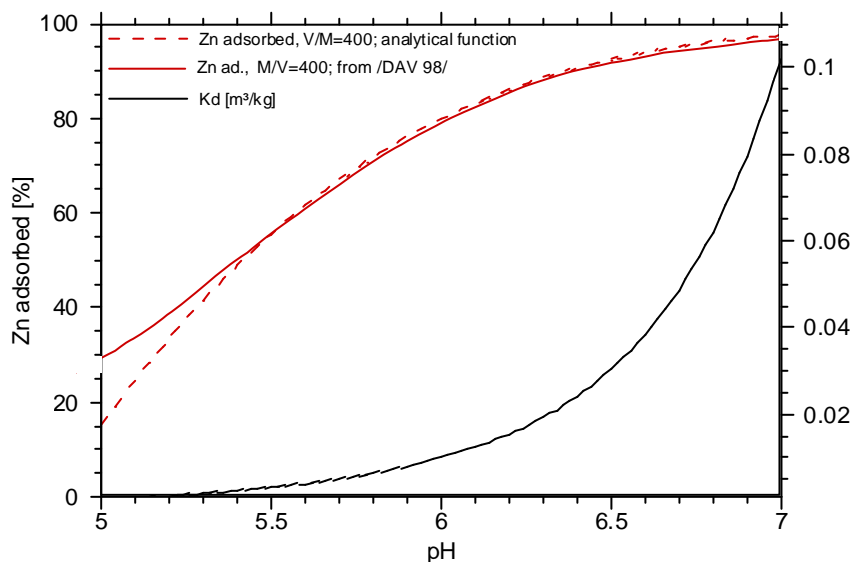


Fig. 3 Approximation of the adsorption (top) and the pH-dependent  $K_d$ -function (lower).

<sup>2</sup> Zinc adsorption on the other hand changes the pH-level only slightly so that the effect of sorption on the pH-value is of secondary importance. It will thus not be considered here.

Fig. 5 and Fig. 6 demonstrate the correlation of low pH-values with a high transport velocity and vice versa. Downwards directed transport due to the recharge is discernable at the top of the model, too. Qualitatively, the model results compare well with the results of [ 7 ]. The most apparent difference is that zinc moves not as fast in the  $r^3t$ -model as in the model from [ 7 ]. This may be attributed to the different degrees of accuracy at which sorption is taken into account in the models. Of course, it has to be shown, too that the assumption of non-retarded protons is valid. However, the effect of the pH-dependent sorption on the zinc transport has been captured.

In the  $r^3t$ -model it is assumed that zinc ceases to pollute the groundwater after 59 years of model time. This terminates the zinc plume. At the same time the pH-value switches back to uncontaminated conditions. This affects the zinc plume since the front of decreased pH-values migrates faster through the domain than the zinc plume.

Finally, a comparison between the results of the model and the measurements at the site in 1997 - two years after shutdown of the facility - is given in Fig. 4. While the simulated zinc plume shows the same characteristic form as the measured one the agreement is not quite satisfying: the faster moving part on top of the plume is too low and is too thick in the model, the slower moving part is too fast. However, the penetration depth of zinc into the domain appears to be in rather good agreement with the measurements.

Apparently, either the pH-controlling processes were still active for quite some time after shutdown of the disposal plant or the changes in the pH-milieu due to shutdown did not propagate downstream unretarded or both. It is thus highly probable that it takes several years of low pH-conditions to produce a zinc concentration peak as the one observed at 280 m downstream.

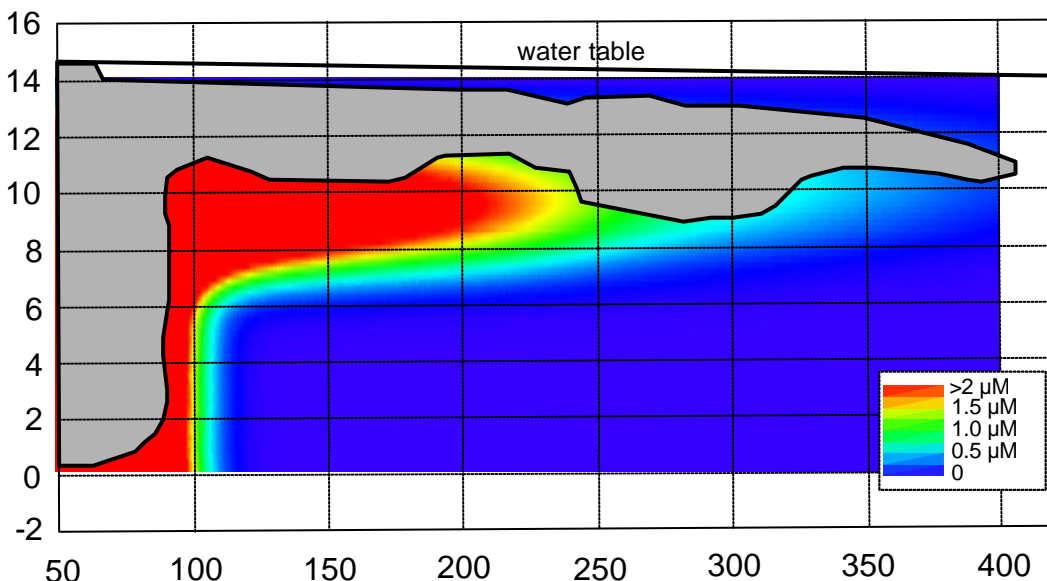


Fig. 4 Zinc concentration after 61 years; measurements from [ 7 ] (isolines representing 0.3, 2, 4 and 8  $\mu\text{M}$  concentration) and  $r^3t$ -model (results in colour) switching back to pristine water conditions after 59 years.

Modelling zinc transport at Cape Cod appears to be a most challenging task. A key process to explain the characteristic form of the zinc plume is the pH-dependent sorption of zinc. In the past a lot of effort has already been invested into the numerical description of this effect and some simplified surface complexation models have been developed so far. Nevertheless, no numerical model up to now simulates the zinc transport at Cape Cod satisfyingly well. The results of the  $r^3t$ -model can therefore not be conformed to compare extremely well with the measurements.

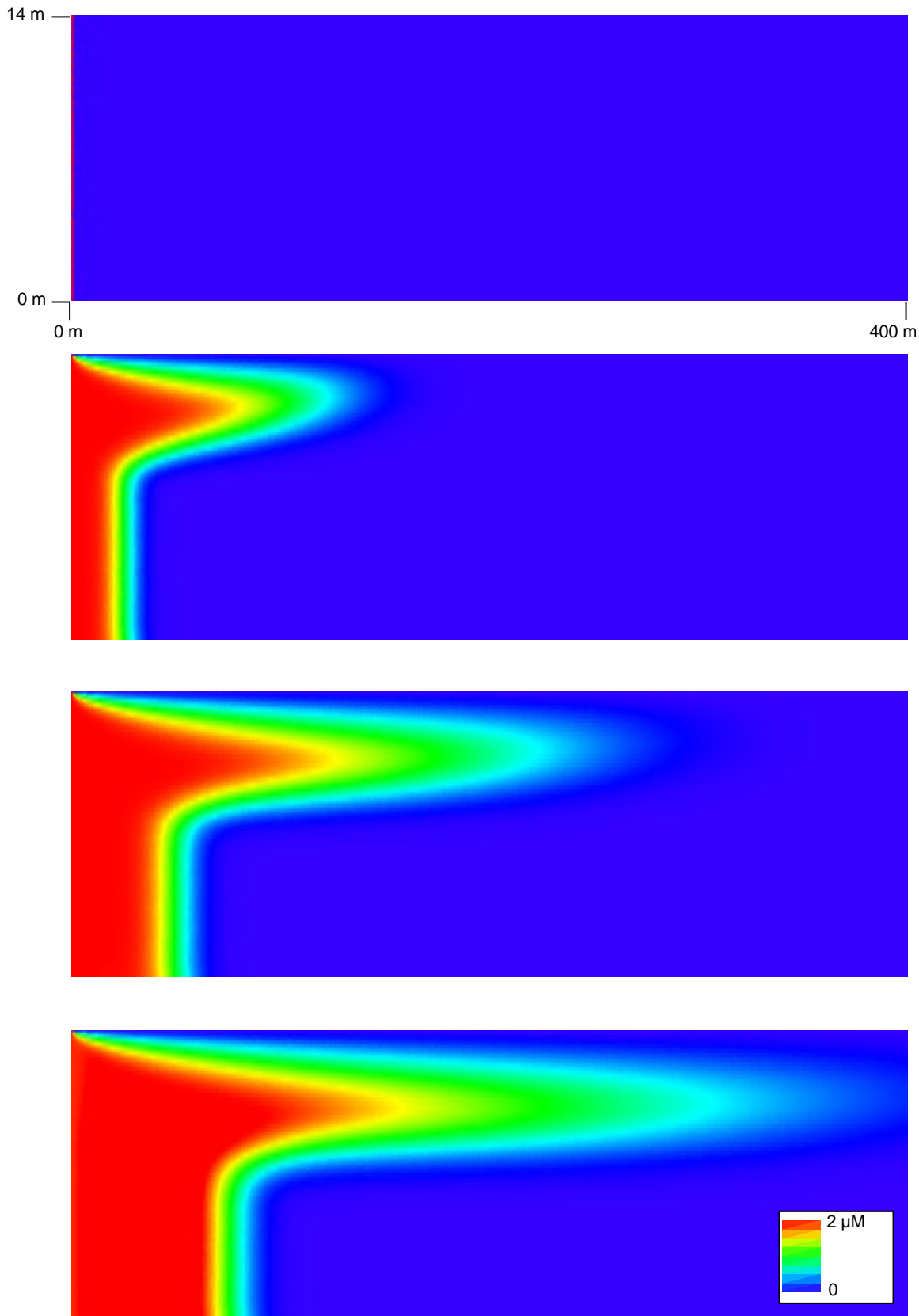


Fig. 5 Simulated zinc concentrations after 0, 20, 40 and 59 years.

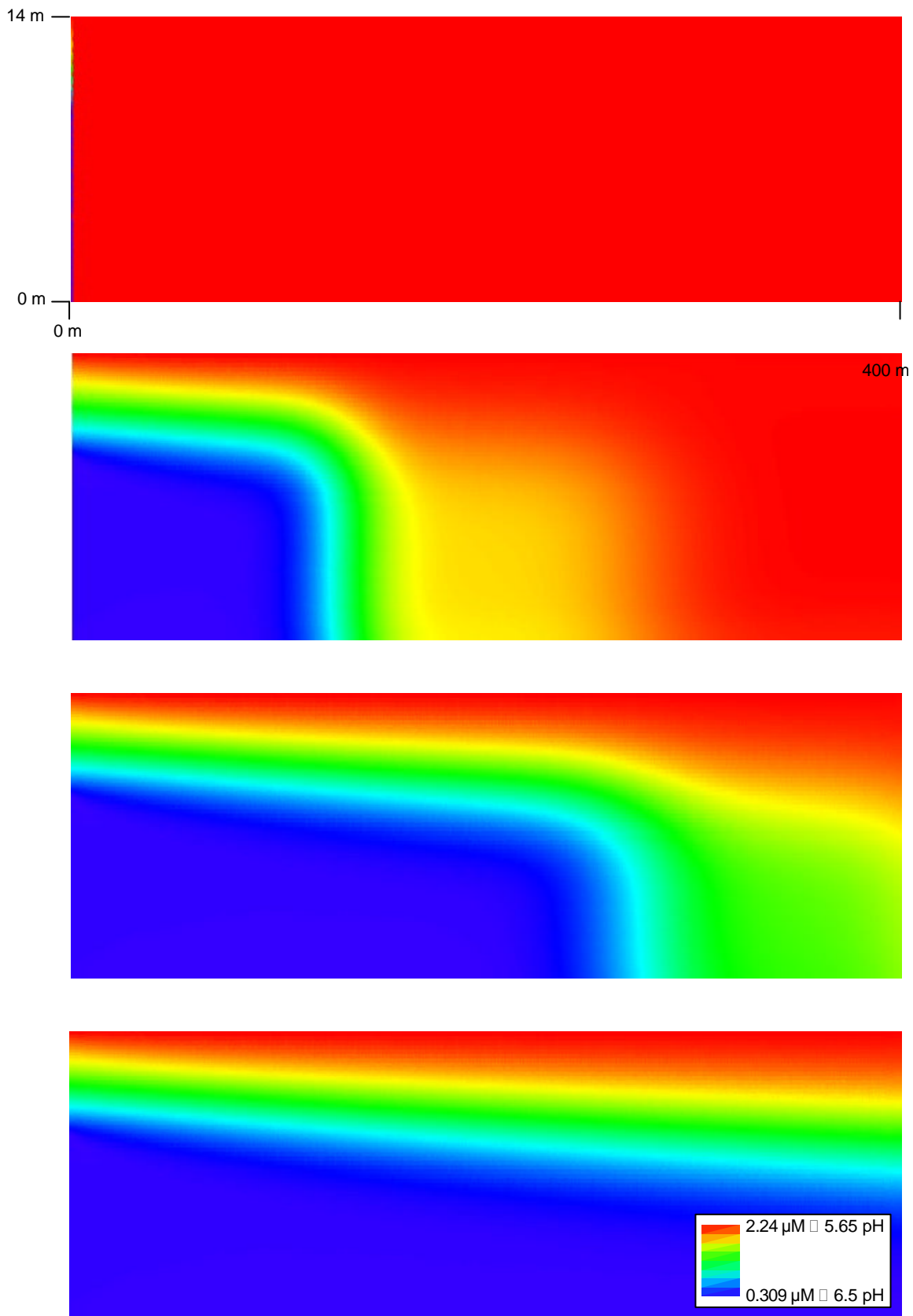


Fig. 6 Simulated proton concentrations after 0, 1, 2 and 3.5 years.

Possibly critical simplifications for the 2D model include the assumption of a constant effluent rate into the ground, the assumption of complete mixing under the sewage disposal beds, isotropy and homogeneity of the flow and transport parameters and the assumption that the pH-value changing quantities can be transported with the flow without ongoing reactions and (at least in case of the  $r^3t$ -model) without retardation.

However, the most meaningful check of the  $r^3t$ -results with respect to the treatment of sorption is a comparison with results of other models. The comparison of the 2-D models clearly shows that the pH-value dependent retardation of zinc is captured in the  $r^3t$ -model. This applies for the time during plant operation as well as for the subsequent period. The model simulated even the drastic increase of the zinc concentration after closure of the sewage plant causing the drop of the pH-value.

Apart from the present work no 3-D simulation has yet been presented in the literature. Modelling results of  $r^3t$  in 3-D for the contamination at the sewage plant are indeed basically the same as for the 2-D model. The only exception are some very localised effects in the mixing zone of contaminated and pristine water. While the 3-D model has only an arguable value for interpreting the situation at Cape Cod, it clearly shows the ability of  $r^3t$  to capture the pH-dependent transport behaviour of zinc even in 3-D.

### 3.2 In-situ diffusion experiments

The transport parameters of radionuclides in clay formations are determined by laboratory experiments in most cases. To verify that the experiments that have been carried out on small scale samples are valid, additional in-situ diffusion experiments are carried out. Accompanying model calculations are performed to interpret the results of the experiments.

The in-situ diffusion experiment DI-A was performed by the Nagra and the Mont Terri Consortium in the Opalinus Clay formation at the underground laboratory of Mont Terri from the beginning of the year 2002 [10]. One aim of this experiment was to test whether the diffusion coefficients measured on small core samples in the laboratory can be transferred to describe the diffusion process on a larger scale in the formation.

To perform this experiment a borehole with a diameter of 76 mm was drilled in the formation. In the borehole an interval of one metre in length was isolated with a packer system. The interval isolated by the packer which is further called test chamber had a volume of  $4.54 \cdot 10^{-3} \text{ m}^3$ . Connected to the test chamber was an external volume, summing up to a total volume of the system to be  $1.09 \cdot 10^{-2} \text{ m}^3$ . The system was filled with a solution with a composition comparable to that of the Opalinus Clay pore water and the solution was equilibrated with the formation in the borehole. After the equilibration was reached, a tracer cocktail of four different tracers was injected in the volume. The layout of the diffusion experiment is schematically shown in figure 7.

In an in-situ borehole diffusion experiment like this, the tracers diffuse through the outer face of the test chamber into the formation. The flux into the formation leads to a drop in the concentration of the tracers in the test chamber. The temporal evolution of the concentration in the test chamber is monitored by taking water samples. After the diffusion experiment is finished an over-core is drilled with a large diameter and the tracer distribution in the formation can be measured on the obtained core material. The temporal evolution of the concentration in the test chamber and the concentration distribution in the formation together allow determining the diffusion coefficient and the diffusion accessible porosity. If only one of both is measured, also only one of both parameters can be determined depending on the estimate of the other parameter.

In the first phase of the DI-A experiment four tracers were injected into the system: HTO, Na-22, caesium in the form of CsCl and iodine in the form of NaI. A detailed description of the experiment and the modelling carried out within the DI-A experiment can be found in [10, 9]. For the modelling within the DI-A experiment the programs GIMRT and

HYDRUS-2D were used. The parameters were chosen according to results from laboratory experiments.

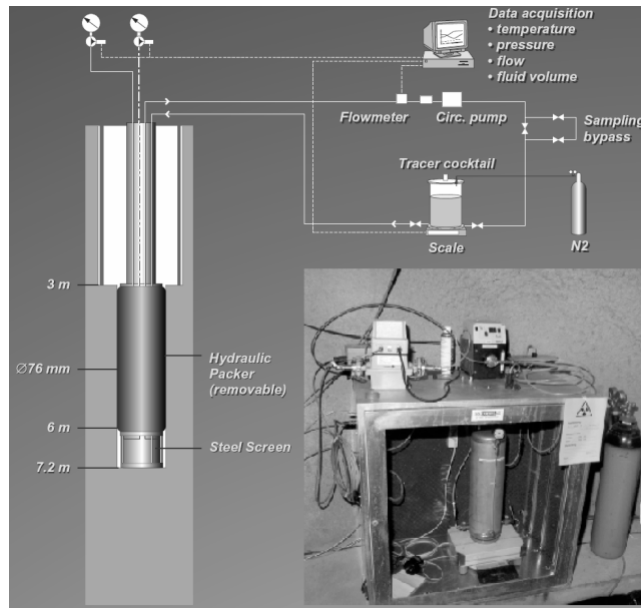


Fig. 7 Schematic representation of the layout of the in-situ diffusion experiment DI-A [ 11 ]

The values of the input data used for the modelling in [ 10 ] are listed in table 1. For iodine anion exclusion was assumed reducing the diffusion accessible porosity by a factor of two. For tritiated water and for iodine no sorption was assumed. Na-22 sorbs with linear and caesium with non-linear sorption isotherm.

Tab. 1: Transport parameters for the modelling of the DI-A experiment

	HTO	Na-22	CsCl	Nal
Injected tracer amount	1,7 MBq	22 kBq	1,835 g	16,34 g
Quantity of substance [mol]	$1,58 \cdot 10^{-9}$	$4,33 \cdot 10^{-12}$	$1,09 \cdot 10^{-2}$	$1,09 \cdot 10^{-1}$
Concentration [mol/m <sup>3</sup> ]	$1,45 \cdot 10^{-7}$	$3,97 \cdot 10^{-10}$	1	10
Half-life [a]	12,323	2,603	-	-
Diffusion coefficient [m <sup>2</sup> /s]	$3,18 \cdot 10^{-10}$	$3,47 \cdot 10^{-10}$	$5,88 \cdot 10^{-10}$	$3,47 \cdot 10^{-10}$
Porosity [-]	0,17	0,17	0,17	0,085
Sorption model	linear Henry	linear Henry	non-linear Freundlich	linear Henry
Sorption parameter	$K_D = 0 \text{ m}^3/\text{kg}$	$K_D = 7,1 \cdot 10^{-5} \text{ m}^3/\text{kg}$	$a = 3,72 \cdot 10^{-4} \text{ mol m}^3/\text{kg}$ $b = 0,53$	$K_D = 0 \text{ m}^3/\text{kg}$

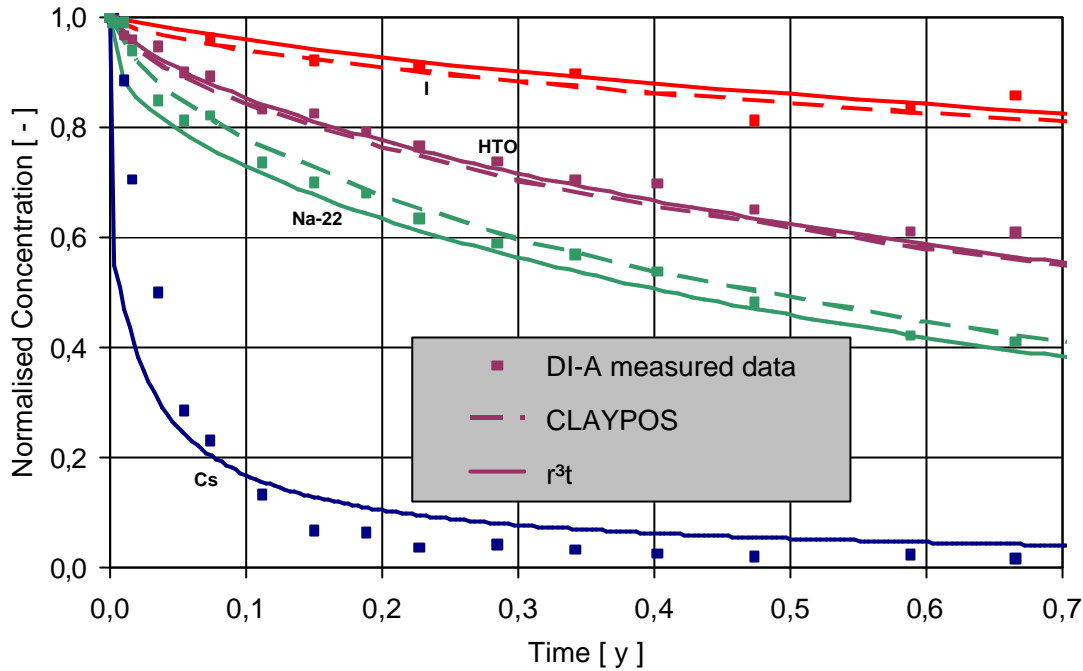


Fig. 8 Temporal evolution of the normalised tracer concentration

To test the program  $r^3t$  the temporal evolution of the concentration in the test chamber and the concentration distribution in the formation was modelled with  $r^3t$  and one additional program called CLAYPOS and the results were compared to the data of the experiment and to the modelling performed within the DI-A experiment. The modelling with  $r^3t$  was performed with a two-dimensional geometry with Cartesian coordinates and the modelling with CLAYPOS was performed with one-dimensional cylinder geometry.

The result of the modelling of the temporal evolution of the concentration in the test chamber with  $r^3t$  and CLAYPOS is shown in figure 8. The profile for caesium could only be modelled with  $r^3t$  since sorption with a non-linear isotherm is not implemented in CLAYPOS. It can be seen that there exist a good correlation between the measured data from the experiment and the modelled data. There is also a good agreement between the modelling with both programs and the modelling within the DI-A experiment presented in [ 10 ]. The differences which can be seen between  $r^3t$  and CLAYPOS are due to the differences in the model geometry and are rated to be not relevant. The modelled concentration distribution in the Opalinus Clay formation - which is not shown here - was also in good agreement to the experimental data and the result from other models.

As result of the modelling of the DI-A diffusion experiment it was found that the modelling with both programs  $r^3t$  and CLAYPOS could be performed successfully. The results fitted well to the experimental data and to modelling results obtained by other groups with different programs.

For test chambers with a smaller interval length the effect of the ends of the interval avoids a correct simulation in a two-dimensional geometry. This is the case in the DR experiment which is described in the following.

The new DR experiment is performed by the Nagra within the framework of the European FUNMIG. The experiment has started in the spring 2006 and the main differences compared to the DI-A experiment are a smaller length of the test interval of 0.15 m and a larger water volume in the circuit of about 20 l. Figure 9 shows the 3D wireframe model of the simulation with  $r^3t$  and the tracer plume. Anisotropy of the diffusion has been taken into account with the diffusion parallel to the bedding being four times higher than perpendicular to the bedding.

This effect can be seen in the shape of the tracer plume in figure 9: The shape is not spherical as it would be expected in an isotropic case, but is elliptic.

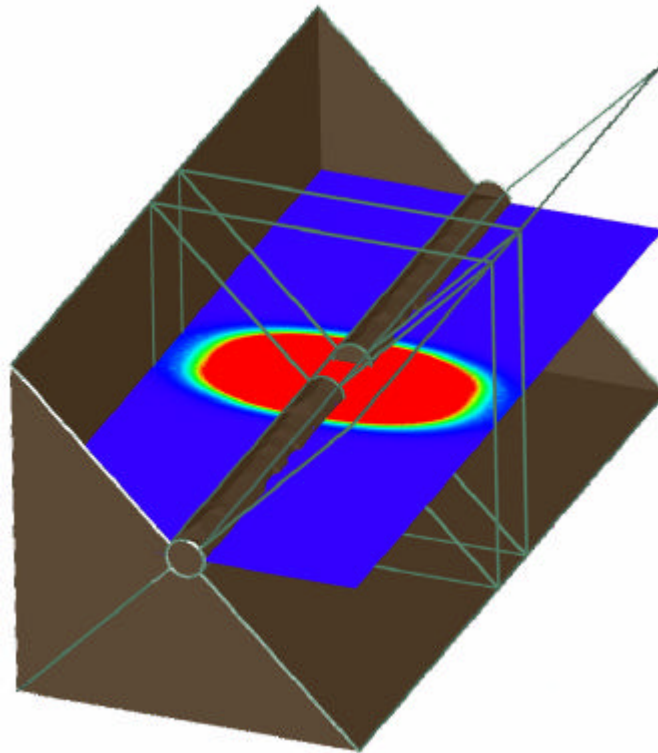


Fig. 9 3D-model of the simulation with  $r^3$

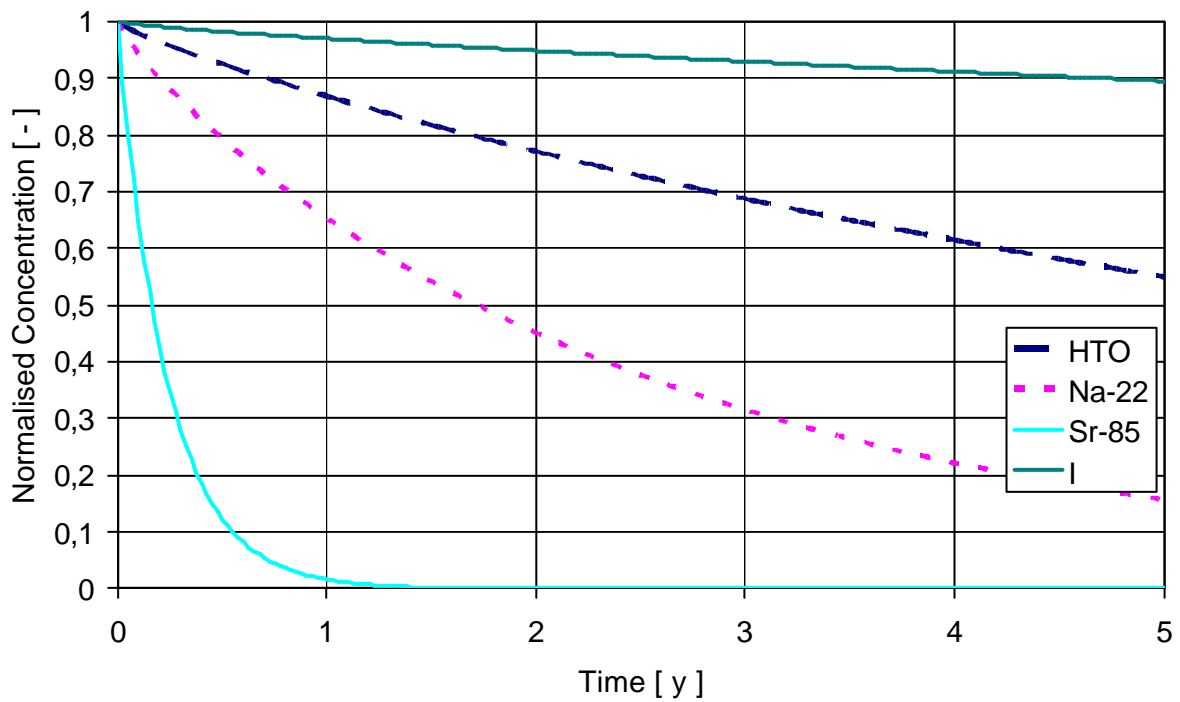


Fig. 10 Predicted temporal evolution of the tracer concentration in the borehole of the DR experiment

The predicted temporal evolution of the tracer concentration in the borehole from the simulation with  $r^3t$  is shown in figure 10. Iodine shows a slow change of the concentration due to a low diffusion coefficient and a low diffusion accessible porosity. Sr-85 on the other side shows a very fast change in concentration which is mainly due to the short half life of Sr-85. It can be further seen that the change in concentration is slower for all tracers compared to the DI-A experiment. This effect is due to the higher circuit- to test chamber volume ratio. No experimental data exists yet to compare the modelling with. The results of the modelling with  $r^3t$  and of three other models by other groups from Europe in comparison with the experimental data will be presented within the FUNMIG project in the near future.

## 4 CONCLUSIONS

Modelling zinc transport at Cape Cod appears to be a most challenging task. However, it has been shown that the modelling of the pH-value dependent retardation of zinc is captured in the  $r^3t$ -model. This applies to the time during plant operation as well as for the subsequent period. The model simulated even drastic increase of the zinc concentration after closure of the sewage plant causing the drop of the pH-value.

As a result of the modelling of the DI-A and DR diffusion experiments it was shown that the modelling with the program  $r^3t$  could be performed successfully. While the experiment DI-A could be modelled with a two-dimensional geometry, for the DR experiment a three-dimensional geometry was needed. The results of the DI-A simulation fitted well to the experimental data and to results of the modelling results with CLAYPOS and by other groups. For the DR experiment the comparison will experimental data and to results from other groups will be performed in the near future within the European project FUNMIG.

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