

SIMULATION OF THE TRANSPORT OF AROMATIC AMINES IN THE UNSATURATED ZONE FOR THE EVALUATION OF AN ENVIRONMENTAL REMEDIATION PROJECT

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ABSTRACT

The T2VOC code was used to evaluate the efficiency of environmental remediation activities planned on a portion of the ex-ACNA area, an industrial site where the Chemical Company ACNA carried out its industrial activity from the end of 1920 up to 1983. First industrial activity started at the end of 19th century. The area is close to Cesano Maderno town, located some 15 km NNW of Milan in Northern Italy.

Since the mid-seventies, part of the study area was used as a landfill for inert materials as well as for surface disposal of contaminated wastes which were then covered with local soil. The chemicals present in the wastes are heavy metals and organic chemicals, with a predominance of aromatic amines. Soil and groundwater analyses showed that the chemicals diffusion through the thick unsaturated zone was already affecting the underlying unconfined aquifer.

Main planned remediation activities included the removal of most contaminated wastes and landfill capping to avoid the infiltration of meteoric water, responsible for the downward transport of chemicals. The T2VOC code was employed for 3-D simulations of the unsaturated zone to evaluate the efficiency of the planned remediation activities in preserving groundwater quality. First the steady state flow field, then a reasonable reconstruction of aromatic amines diffusion over the previous 20 years were simulated. Finally, the forecast of aromatic amines transport evolution was simulated, both in the absence of any remediation, as well as after the execution of planned remediation activities.

INTRODUCTION

The study area represents the southern portion of the Cesano Maderno chemical complex run by ACNA SpA company and closed down in 1983. During the past activity many different productive activities took place in

the area and several companies are still using the area for their chemical productions. The study area shown in Fig.1 was never employed for production activities but, starting from the early seventies, was used for the surface disposal of inert and contaminated wastes. These landfills were located mainly in ground surface depressions previously created by the exploitation of a clay layer which initially covered most of the area. The shaded areas in Fig. 1 represent the main discharge locations: zone 2, located East, and zones 3 and 4, located West of Garbogera stream; zone 6 located on the West side of the area.

Fig. 1 also shows 7 basins which were used for approximately ten years since the mid-seventies for the thickening of industrial muds derived from chemical processes which included the production of pigments and colorings.

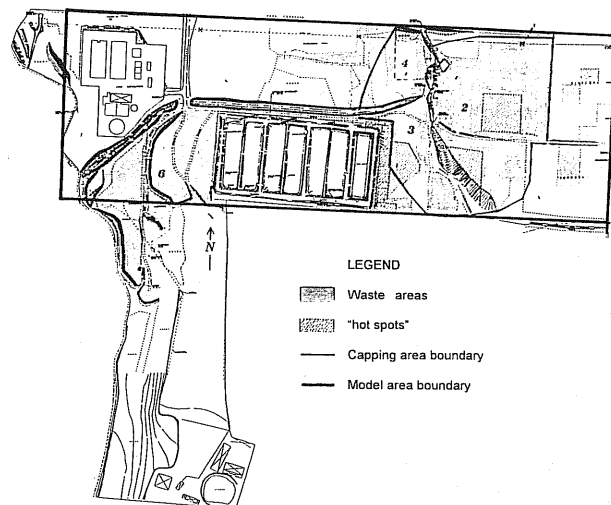


Fig. 1 The Cesano Maderno ex-ACNA site. The waste areas and the model grid location are shown.

The chemicals present in the wastes are heavy metals and organic chemicals, with a clear predominance of aromatic amines. Whereas heavy metals predominate in zone 6, aromatic amines have been identified as the most important compounds in zones 2, 3 and 4 as far as possible groundwater contamination is concerned. As an important unconfined aquifer is present in the area, starting in the early nineties a series of investigations were performed on different locations of the chemical complex area in order to define the local geology and hydrogeology, identify the contaminant species present in the soil and in groundwaters, and reconstruct their distribution. The surveys led to the identification of priority zones for which immediate remediation projects were requested by control Authorities. EniChem SpA was asked to provide for the general setting of the area shown in Fig. 1. This included the remediation of zone 6, of the basins area, of zones 2,3 and 4, and the construction and operation of an hydraulic barrier downstream of the chemical complex. EniChem entrusted Aquater with the design of remediation activities and the execution of contaminant transport simulations to confirm the effectiveness of the planned activities in preventing pollution in the unconfined aquifer (Aquater, 1997). This paper describes the modeling studies performed to verify the effects of the remediation project designed for zones 2, 3 and 4 located in the eastern portion of the area.

GEOLOGICAL AND HYDROGEOLOGICAL BACKGROUND

The study area is located in the Upper Lombardian plain that lies within the Po River Valley. The local stratigraphy was reconstructed by means of over 200 wells and boreholes drilled both for industrial water supply and during the above mentioned surveys. Starting from the ground surface the following stratigraphy was encountered:

- a. weathered clay layer, made up by a reddish silts and clays layer up to 5 m thick, known as "Ferretto";
- b. fluvioglacial deposits, consisting of sands and gravels with silty-clay lenticular interbeddings, down to 25 to 30 m from ground level, within a silty-sandy matrix;
- c. sands and gravels with low cemented conglomerates and sandstone interbeddings down to about 40 m from ground surface, where the top of an almost continuous silty-clay layer is encountered, with thickness ranging from 1 m to 3 m.
- d. alternating sand and gravel layers with lenticular cemented levels interbedded down to about 70 m below ground surface;
- e. clay layer extending over the entire area with thickness ranging from a few meters to some tens of meters. It represents the top of a confined regional aquifer having an average thickness of some 30 meters.

The confined aquifer is not locally affected by contamination. Above it, an unconfined aquifer, located in the d. unit mentioned above, is present with average water level some 60 m below ground level. Groundwater flows in a SE direction. The area is thus characterized by a thick heterogeneous unsaturated zone. Above the silty-clay layer at 40 m depth, a saturated zone was detected. Its thickness, ranging from a few tens of centimeters up to a couple of meters, varies throughout the year depending on meteoric recharge and the recharge operated by the two surface streams: the Lombra river which borders the west side of the study area, and the Garbogera stream which divides zones 3 and 4 from zone 2. The piezometric surface of this perched saturated level was observed over the central portion of the study area with a general NS flow direction.

Depending on the presence of low permeability lenses, scattered saturated levels were also encountered in the first 30 m.

PLANNED REMEDIATION MEASURES

The surveys performed on zones 2, 3 and 4 pointed out the presence of a consistent amount of wastes having quite variable concentrations of contaminants and the presence of chemicals at depths which make the removal of contaminated soil unfeasible. Thus, the remediation project was based on a series of integrated activities including:

- complete removal of the most contaminated hot spots from the 3 zones (dashed areas in Fig.1);
- capping of the surface occupied by wastes (the shaded area in Fig.1) and the construction of a lateral impervious trench from the ground surface down to the top of the surface clay layer (Ferretto);
- impermeabilization of the whole Garbogera stream bed to avoid further infiltration of stream water into the unsaturated zone.
- impermeabilization of the ponds area shown in Fig.1;
- removal of small amounts of wastes located outside the capping area and their transport inside the capping area.

NUMERICAL MODEL SET UP

In order to assess the planned remediation activities, the control Authorities requested the evaluation of the expected reduction of contaminant flux through the unsaturated zone. They asked to verify that the concentration of specific contaminants be maintained below given limits, defined accounting also for a safety factor. They requested to compute the concentration in the unconfined aquifer through a simple mass balance using the evaluated aquifer natural flow and the computed contaminant flux through the unsaturated zone and assuming instantaneous mixing. According to their

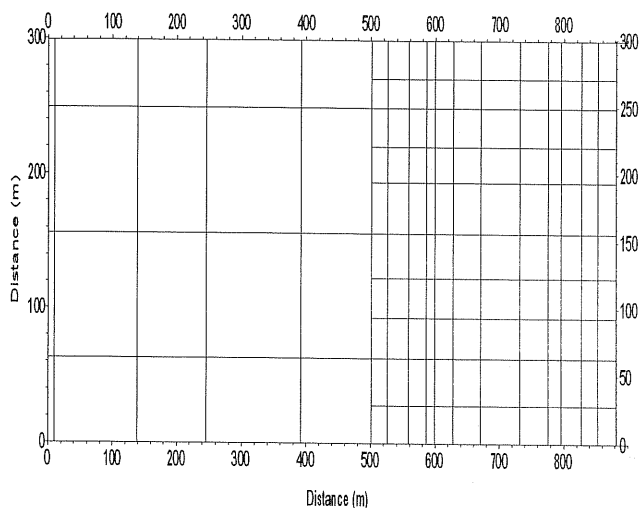


Fig. 2 Model grid layout showing the grid refinement on the east side.

specifications, the model grid included only the unsaturated zone, whereas the unconfined aquifer was simulated as a constant pressure boundary. The extension of model grid is shown in Fig.1: it covers all 3 zones of interest: zones 2, 3 and 4, and is extended westwards up to the Lombra river to account for its possible recharge of the perched saturated level.

Fig. 2 shows grid discretisation on the horizontal plane: the grid extends for 882 m EW and for 299 m NS. It is made up of a main grid, called grid A, of 4 x 9 elements and 20 layers. On the east side and limited to the first 10 m, a grid refinement was included to properly account for the more detailed knowledge of zones 2, 3 and 4, acquired through the drilling of shallow boreholes on a regular mesh of about 30 m side. The main grid has 560 elements and the refinement has 1200 elements for a total of 1760 elements.

Considering that a sub-vertical flow direction prevails in the unsaturated zone, impervious lateral grid boundaries were assumed. Bottom boundary is held at constant pressure to represent the unconfined aquifer water level, whereas the upper boundary is held at atmospheric pressure using inactive elements. The ground surface and the Ferretto clay layer morphology were followed to accurately reproduce the spatial distribution of wastes disposed of in zones 2, 3 and 4. The vertical grid discretisation and an example of different rock domain distribution is shown in Fig. 3, where a WE vertical section through the third slice of grid A and the sixth slice of grid B is represented. This representative section, referred to as section A3-B6, crosses the central part of zone 2 where the largest layer of wastes and the highest concentration of chemicals were found.

The rock domain properties were partially defined using site measurements such as permeability tests in the unsaturated zone, pumping tests in the unconfined aquifer, and laboratory tests on undisturbed samples collected in clay and silty-clay levels. Grain size analysis and water content determinations were extensively performed on coarse sediment samples collected in the unsaturated zone in the attempt to use published correlations and suggested properties ranges. In particular the range of aqueous phase saturation was estimated from the water content, assuming reasonable values of rock porosity according to the observed lithology. The Van Genuchten (1980) model was used for the capillary pressure whereas the Stone first model (1972) implemented on the T2VOC code was used for the relative permeability correlations.

SIMULATION OF NATURAL STATE

The modeling study was performed using the T2VOC computer code developed at LBNL (Falta et al., 1995), assuming constant temperature for every simulation.

The first step was the reproduction of a reasonable natural state which included the evaluated meteoric recharge, the evaluated recharge from surface streams, the observed water level of perched aquifer at 40 m depth, and the presence of a perched saturated level in zone 2, located above the Ferretto clay layer at the bottom of the wastes.

In order to reproduce the above data and the evaluated water saturation distribution with depth, several runs were made using mainly the permeability and relative permeability of rock domains as matching parameters.

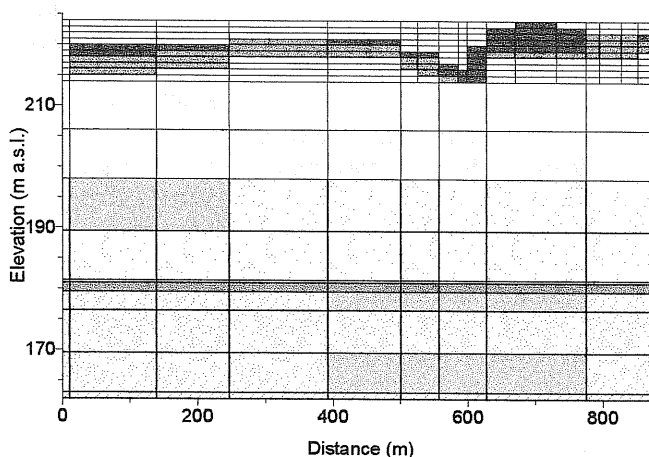


Fig. 3 A2-B6 vertical section showing the discretisation grid and the rock domain distribution.

Main result of the natural state simulation was the indication of the effect of the Garbogera stream in determining a concentrated vertical flow both because of its direct recharge and because of the drainage operated by the stream bed which cuts the Ferretto clay layer and thus determines horizontal flow components from zones 2, 3 and 4.

AROMATIC AMINES DISTRIBUTION

Most of material disposed of in the area during the seventies is contaminated at different degrees by organic compounds and heavy metals. Organic compounds are the most important chemicals in zones 2, 3 and 4 as far as the contamination of ground water is concerned. Among them the aromatic amines, which were used for the production of pigments, were by far the most abundant. About 30 different amines were identified in the wastes. According to National Italian regulations, the aromatic amines are assigned to different classes depending on their known, or assumed toxicologic effects. In order to simulate the effects of the planned remediation activities in the presence of multiple contaminants, we made reference to the aromatic amines of class 1, defined as very toxic with cumulative effects. Public Italian regulations do not specify the concentration limits for the aromatic amines. For the modeling study, we assumed for the aromatic amines of class 1 the maximum acceptable concentration in ground water specified for pesticides: 0.1 ppb. For the present project a safety factor of 4 was requested (Provincia di Milano, 1995), thus the concentration in ground water of class 1 aromatic amines had not to exceed 0.025 ppb. We used at any sampling point, the sum of concentrations of aromatic amines of class 1, whereas the transport properties of N,N-diethylaniline (CAS number 91-66-7) were used to simulate all the class 1 aromatic amines. The measured average concentration of class 1 aromatic amines was determined and assigned to each rock domain. When greater than the average value plus the mean deviation, the measured concentration was assigned to single elements to reproduce the presence of the so called 'hot spots'. The variation of measured concentrations with depth was also accounted for.

The N,N-diethylaniline is a toxic aromatic amine characterized by low water solubility, relatively low saturation pressure, and limited adsorption on organic carbon. In particular, both the water solubility and the octanol/water partition coefficient (K_{ow}) were experimentally determined at the laboratory. The organic carbon/water partition coefficient K_{oc} was then computed from the K_{ow} using an empirical correlation for dinitroanilines and pesticides given by Olsen and Davis (1990). To check the reliability of computed K_{oc} , laboratory batch tests were also performed on soil

samples collected at different depths to experimentally determine the solid-aqueous distribution coefficient K_D . As we found experimental K_D values systematically higher than the value computed according to the estimated K_{oc} value and measured fraction of organic carbon f_{oc} , we decided to use the computed K_{oc} evaluated from the K_{ow} . This choice was also justified by the difficulties encountered in reproducing the conditions present at the field during laboratory testing. In order to account for the long-term effects of molecular diffusion in the aqueous phase when the advective flow becomes negligible, the molecular diffusion in liquid phases was included in a fashion similar to that used for the EOS7R module of TOUGH2 (Oldenburg and Pruess, 1995). Considering the low concentration of chemicals, for all the simulations the value of the convergence criterion for relative error was decreased from the default value of $1E-5$ to $1E-8$.

The measured distribution of contaminants in the waste materials was quite variable and fairly dependent upon natural transport processes, as it depends on the initial concentration of contaminated wastes and the procedure followed during disposal at the site. Thus, it was necessary to input the observed concentration of contaminants for each element in the obtained natural state run. They were available on a mass fraction basis referred to the total mass of soil including the moisture content, whereas T2VOC requires the molar fraction of chemicals in the aqueous or gaseous phases according to the combination of phases present. The code was slightly modified to read initial chemical concentrations given in ppm over total mass and to convert them internally into the appropriate primary variable according to local porosity, water phase saturation and the mass fraction of organic carbon. The f_{oc} distribution was also determined by means of laboratory analysis both on soil and waste samples and accordingly used in the model.

SIMULATION OF PREVIOUS CONTAMINANT TRANSPORT

The reconstruction of site history pointed out that the disposal of wastes in zones 2, 3 and 4 began during the mid-seventies. Organic chemicals characteristic of the study area had already been detected in the ground water, proving that the transport of organic chemicals through the thick unsaturated zone had already affected the unconfined aquifer. On the other hand, the concentration distribution of organic chemicals was reasonably reconstructed only down to about 20 m depth, both because of the high costs involved and the decrease in chemicals concentration with depth, often below the detection limit of analytical methods used. The simulation of chemicals transport in the previous 20

years was then performed following the steps described below:

1. Simulation of chemical transport for 20 years through the unsaturated zone driven by infiltrating meteoric water and recharge from surface stream using the chemical distribution measured in the upper 20 m. Determination of the amount of chemicals flowing into the unconfined aquifer.

2. Considering that all the chemicals were initially contained only in the wastes, the estimated initial amount of chemicals was distributed among the elements representing the wastes, proportionally to the concentration measured in 1996.

3. The transport of chemical was then simulated from 1976, considered as the approximate beginning year, to 1996 using the reconstructed reasonable initial distribution of chemicals. The fraction of organic carbon was the only matching parameter used to reproduce the average chemical concentration measured in groundwater in 1996 downstream from the study area. It was slightly increased compared to the measured average values for deep rock domains for which limited experimental data were available. With respect to the measured distribution, the computed chemical distribution in 1996 pointed out the role of Garbogera stream in producing preferential downward flow of chemicals transported by the infiltrating water. This is clearly shown in Fig. 4 which presents the simulated concentration of chemicals in 1996 on the vertical section A3-B6 (concentrations are in ppm over total mass).

The simulated chemical distribution in 1996 represented the initial conditions for the forecast of chemical flux into the unconfined aquifer for additional 80 years in the absence of any remediation activity and following implementation of the planned remediation project.

FORECAST OF AROMATIC AMINES TRANSPORT

The forecast of chemical flux through the unsaturated zone was then performed both in the absence of interventions (no-actions option) and accounting for the described remediation measures. The simulation was extended for a period of 80 years from 1996 to 2076. The computed average concentration in the unconfined aquifer, assuming instantaneous mixing, is shown in Fig. 5 for the two different simulations as a function of time. With no remediation activities, the average chemical concentration in groundwater is expected to increase with time, reaching 1 ppb after about 30 years from the beginning of transport and 3 ppb after 100 years. As the target concentration is only 0.025 ppb, the simulation clearly pointed out the need to undertake remediation measures.

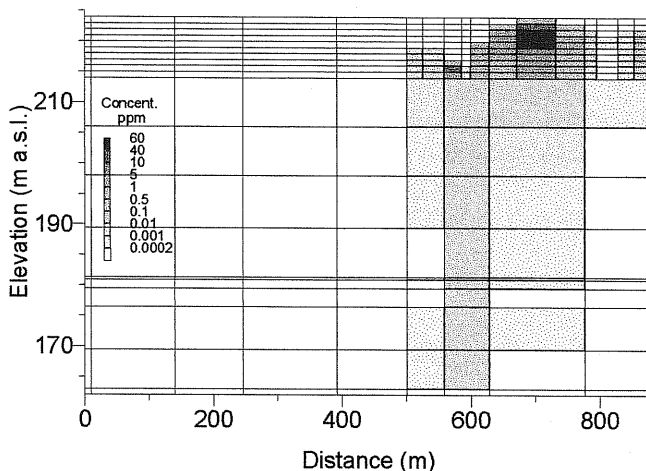


Fig. 4 Simulated *N,N* diethylaniline concentration in soil on the vertical section A3-B6 (year 1996).

When the effects of the planned remediation project were accounted for, the concentration of chemicals in ground water declined consistently during the first ten years owing to the reduction of water flow through the unsaturated zone due to surface capping. The concentration trend then flattens around a value of 0.02 ppb showing an increase at late time after about 50 years. The residual chemical flux is due to the reduction of water phase saturation below the capped area towards a gravity-capillarity equilibrium in the absence of recharge, and to the effects of lateral flows above the clay layer at 40 m depth which can convey the chemicals reaching this depth further downwards.

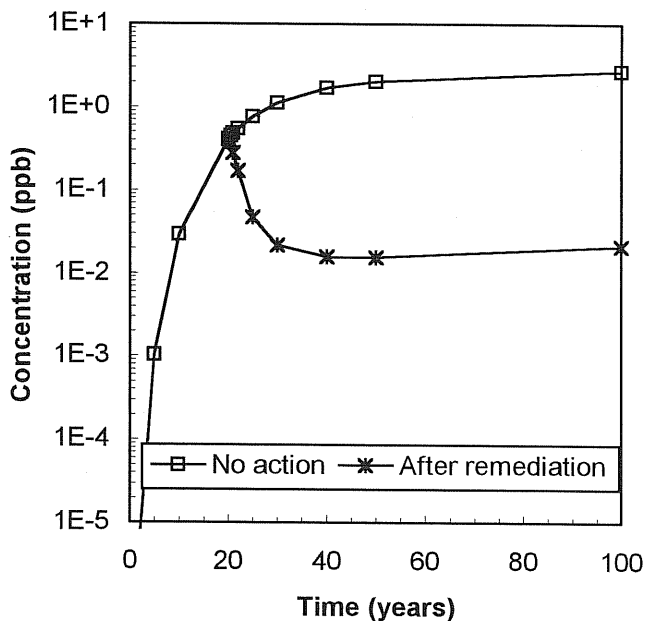


Fig. 5 Forecast of chemical concentration in ground water with and without the planned remediation

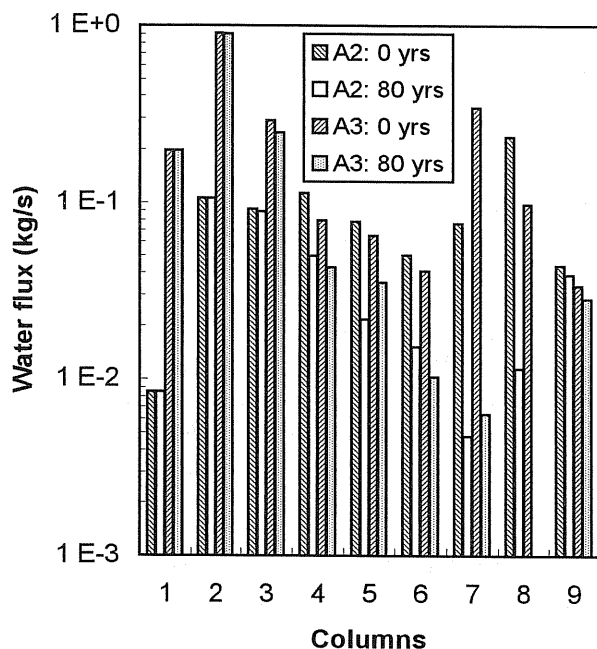


Fig. 6 Reduction of water flux across the water table after 80 years since the surface capping on vertical sections A2 and A3.

The presence of residual fluxes 80 years after the capping is clearly shown in Fig. 6 where the residual aqueous phase flux entering the aquifer surface is compared with the undisturbed flux on two vertical sections: the A2 and A3 sections. Fig. 6 shows that the capping mainly affects the grid columns from 4 to 8, with marginal influence on the other columns. The greatest effects are felt on columns 7 and 8, where most of wastes are located.

As regards the suggested increase of groundwater concentration at late time, it must be pointed out that the possible biodegradation of chemicals was neglected. This choice was based on the lack of reliable data regarding the biodegradation features of aromatic amines, and considering that conservative results were obtained in this way. Additional simulations considering a half life in the order of 100 years with the biodegradation described by the first order model presently implemented in the T2VOC code, suggested that no increase of chemical concentration at late time should be expected.

CONCLUSIONS

The simulation of chemical transport through the unsaturated zone after the execution of planned remediation activities confirmed the effectiveness of the designed measures in limiting future contamination of the unconfined aquifer.

Despite the complexity of hydrogeology in the thick unsaturated zone present in the subsurface of the study area, and the difficulties encountered in achieving proper characterization of this heterogeneous system, the numerical simulations provided a reasonable quantitative assessment of the effects of planned remediation activities.

As far as the performances of the T2VOC code are concerned, the study pointed out the need for a meshmaker capable of generating grids that follow the shape of sloping layers of varying thickness, in order to properly account for the sub-horizontal flow components that can occur in the unsaturated zone when low permeability sub-horizontal layers are present.

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