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INVESTIGATION AND REMEDIATION OF DNAPL-POLLUTED AQUIFERS-GENERAL INFORMATION AND CASE HISTORIES OF HESSEN/GERMANY

02-0166

Investigation and remediation of DNAPL-polluted aquifers

- general information and case histories of Hesse/Germany -

Benedikt Toussaint[*]

1.   Introduction in the problem

Non-aqueous phase liquids, the so-called NAPLs, are a challenge for each hydrogeologist or engineer because these organic substances occur in several phases in the underground (as free product, gaseous, dissolved in water, and adsorbed on solid particles). Groundwater monitoring and usually subsequent remedial activities require an understanding of complex processes affecting fate and transport of contaminants in the subsurface environment as precondition for effective and cost-saving investigation and remediation.

NAPLs are divided into two classes: those that are lighter than water (LNAPLs) and those with density greater than water (DNAPLs). LNAPLs include hydrocarbon fuels such as gasoline, heating oil, kerosene, jet fuel, and aviation gas. DNAPLs include 1,1,1-trichloroethane, carbon tetrachloride, chlorophenols, chlorobenzenes, tetrachloroethene, and polychlorinated biphenyls (PCBs).

Contrary to the LNAPLs that float on top of the capillary fringe or on the water table, the high density of DNAPLs provides a driving force that in combination with low viscosity and low interfacial tension can carry them deep into aquifers. Because soil and rock material will bind these compounds only weakly, thus they are very mobile in the underground and are part of the „chemical zoo", over long time underestimated with regard to its hazardous potential.

This paper lays emphasis on aliphatic chlorinated DNAPLs with one or two C-atoms with simple or double bonding and chlorine components. Because the DNAPLs have exceptionally good properties for their intended uses, especially as organic solvents, very large quantities of these (environmental) chemicals have been, and continue to be produced, transported, used, and disposed of by many sectors of our modern society (table 1). Given the properties of these compounds (table 2), it is not surprising that chlorinated solvents are ubiquitous groundwater contaminants in nearly all urban or suburban areas not only in the industrialized world. Although the clorinated solvents have low absolute solubilities, the resulting water contamination will typically be greatly in excess of its drinking water concentration limits (10 µg/l). Therefore, incorporated with the drinking water they contain health risks, they are harmful, toxic and sometimes they cause cancer.

Historically, it was believed that these substances released to the unsaturated zone would easily and entirely volatilize to the atmosphere. In reality, a part of these releases will be transported into the subsurface by gaseous diffusion or gravity, by infiltration of contaminated water, and as moving DNAPL phase, and, once contamination reaches the saturated zone high volatility is of little assistance in removing the DNAPLs because transport across the capillary fringe can be exceedingly slow.

[*] Address of author: Prof. Dr. B. Toussaint, Hessian Agency for the Environment and Geology, Rheingaustrasse 186, D-65203 Wiesbaden/Germany
phone: +49/611/6939709, fax: +49/611/6939555, e-mail: b.toussaint@hlug.de

Table 1:   Principal uses of the major chlorinated solvents (examples)

• Chemical production and distribution solvents, recycled solvents, dyes and paints, plastics and polymeres, pesticides • Manufacturing uses general metal fabrication, tool and die making, aircraft production, electronics/electrical fabrication, automobiles and parts production, printing, metal cleaning/degreasing, paint removal/stripping • Service uses Commercial and retail cleaning, car repair, food processing (e.g. decaffeinated coffee)

Table 2:   Properties of selected DNAPLs

SUBSTANCE						
IUPAC nomenclature	dichloro-methane	1,1,1-tri-chloro-ethane	tetrachlo-roethene	trichlo-roethene	cis 1,2-dichloro-ethene	hydro-genoxide (water)
chemical formula	CH_2Cl_2	$C_2H_3Cl_3$	C_2Cl_4	C_2HCl_3	$C_2H_2Cl_2$	H_2O
molecular mass [g/mol]	84.93	133.41	165.83	131.29	96.94	18.02
density at 20°C [g/cm^3]	1.33	1.34	1.62	1.46	1.28	0.99
solubility in water at 20°C [mg/l]	20,000	1,300	160	1,090	800	-
vapour pressure at 20°C [Pa]	47,300	13,300	1,860	7,800	23,400	2,340
boiling point at 1013 hPa [°C]	40.6	74.1	121.2	86.7	60.3	100.0
diffusion coefficient in air at 25°C and 1013 hPa [cm^2/s]	0.1037	0.0794	0.0797	0.0875	0.0911	no data found
dielectric constant at 20°C	8.9	7.1	2.3	3.4	9.3	81.6
partition coefficient water/air at 20°C	8.10	1.68	1.22	2.74	0.51	-
partition coefficient n-octanol/water at 20°C	17.8	309	398	195	30.2	-
surface tension of liquid phase at 20°C [mN/m]	26.5	25.6	31.7	29.3	28.0	73.0
dynamic viscosity at 20°C [mPa·s]	0.43	0.86	0.54	0.57	0.47	0.89

Table 3:   Source types for chlorinated solvent contamination of groundwater (examples)

- leaking underground or above-ground storage tanks
- leaking barrel storage areas
- leaking product pipes
- leaking sewers
- leaking unproperly protected degreasing baths and distillation plants
- leaking buried chemical distribution pipelines
- spillage during highway accidents and train derailments
- intentional disposal into the subsurface in various ways, including
  -domestic septic tile fields (due to solvent-containing cleaning fluids)
  -municipal landfills
  -chemical waste disposal landfills
  -settling ponds and lagoons
  -injection well disposal of either used liquid solvents, or contaminated liquids

The DNAPL groundwater contamination originates mostly in waste disposal and chemical spill sites (table 3).

Three case histories in the region of Frankfurt/Hesse/Germany are presented with the intention to give an overview of the sampling procedures for soil, soil gas and groundwater, and remediation activities in a porous aquifer (Frankfurt Airport) related to fluviatile sands and gravels of Quarternary, fractured aquifer (City of Dreieich, south of Frankfurt) related to Upper Permian (Old Red) sandstones, and karstic aquifer (City of Hadamar, north of Frankfurt), related to Middle Devonian limestones.

2   Behaviour of the DNAPLs in the underground

Different factors either facilitate or inhibit DNAPL penetration through the vadose and saturated zones of an aquifer (table 4).

If a small amount of DNAPLs is spilled the organic substances will flow through the unsaturated zone under the influence of gravity, flowing until reaching residual saturation. Residual DNAPLs can be dissolved by infiltrating water and be transported to the water table, resulting in a contaminant plume within the aquifer.

The residual saturation provides in porous media a large surface area for volatilization usually controlled by molecular diffusion.. When vapour concentrations in the vicinity of the source zone are at saturation, then the vapour transport can be density-driven by gravity. This means a faster vapour sinking and longer spreading distances than by diffusion alone. Vapours can be dissolved by infiltrating water and thus resulting in a contamination of groundwater.

If the spilled amount of DNAPLs is greater than the residual saturation capacity of the unsaturated zone, the organic phase begins to penetrate the saturated portion of the aquifer. DNAPLs are then dissolved by groundwater passing through the contaminated area, resulting in a contaminant plume. Very often, the length of a contaminant plume may reach several kilometers and a width of some 100 meters depending on the shape and size of the source

zone strongly influencing the plume dimensions. The plume terminates at hydrologic boundaries such as rivers or hydraulically effective faults, or productive water wells.

Table 4: Factors which either facilitate or inhibit DNAPL penetration through the vadose and saturated zones of an aquifer

Factors facilitating DNAPL penetration through the subsurface	Factors inhibiting DNAPL penetration through the subsurface
high density	low density
low interfacial tension (surfactants or miscible co-solvents such as methanol, ketone or acetone in the DNAPL; complex DNAPL mixtures)	high interfacial tension (relatively pure chemical products)
low viscosity	high viscosity (DNAPL mixtures with high concentrations of high molecular weight hydrocarbons)
large volume release (disposal of bulk liquid wastes in landfills, lagoons; catastrophic spills and on-going leakages)	small volume release (small spills and leaks)
large duration releases (disposal of bulk liquid wastes in landfills, lagoons; on-going leakages)	short duration releases (small one-time spills and leaks)
high permeability (sand, gravel, fractured rock)	low permeability (unfractured silt and clay aquitards; unfractured hard rock)
vertical and sub-vertical geological structure (angled beddings in sandy aquifers; fractures, fissures, erosional windows in fine-grained aquitards; fractured rock)	horizontal geological structure (horizontal bedding in sandy aquifers; horizontal silt and clay aquitards; horizontal bedding plane partings in sedimentary rock)

Even if larger amounts of DNAPLs are spilled they can reach the bottom of the aquifer, forming pools in depressions. If the impermeable lower boundary is sloping, DNAPLs flow down the dip of the boundary. This direction can be up-gradient from the original spill area if the impermeable boundary slopes in that direction. Flow along impermeable boundaries can spread contamination in directions that could not be predicted based on hydraulics.

The residual saturation capacity of porous media, especially of silt and clay, is much greater than that of fractured hardrocks. Depending on fracture aperture, number and type of fracture connections and the height of the column of continous DNAPL the depth, to which DNAPLs penetrate in fracture networks can be greater than 1000 meters (fig. 1).

Pools of free product solvents are found only rarely even when their existence is not in doubt. The reasons are that conventional site investigation techniques are not well-suited for their detection and the large number of boreholes necessary to encounter small size pools is usually not practical.

Large critical heights are required for DNAPLs to move through unfractured, saturated silts and clays. Thus, these types of materials in many cases may be effective geologic barriers to

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the movement of DNAPLs. An accidental spill, for instance caused by a crash of a truck transporting a large volume of solvents throughout the country, can exceed the critical heigh and, thus, result in a pollution of the underlaying aquifer.
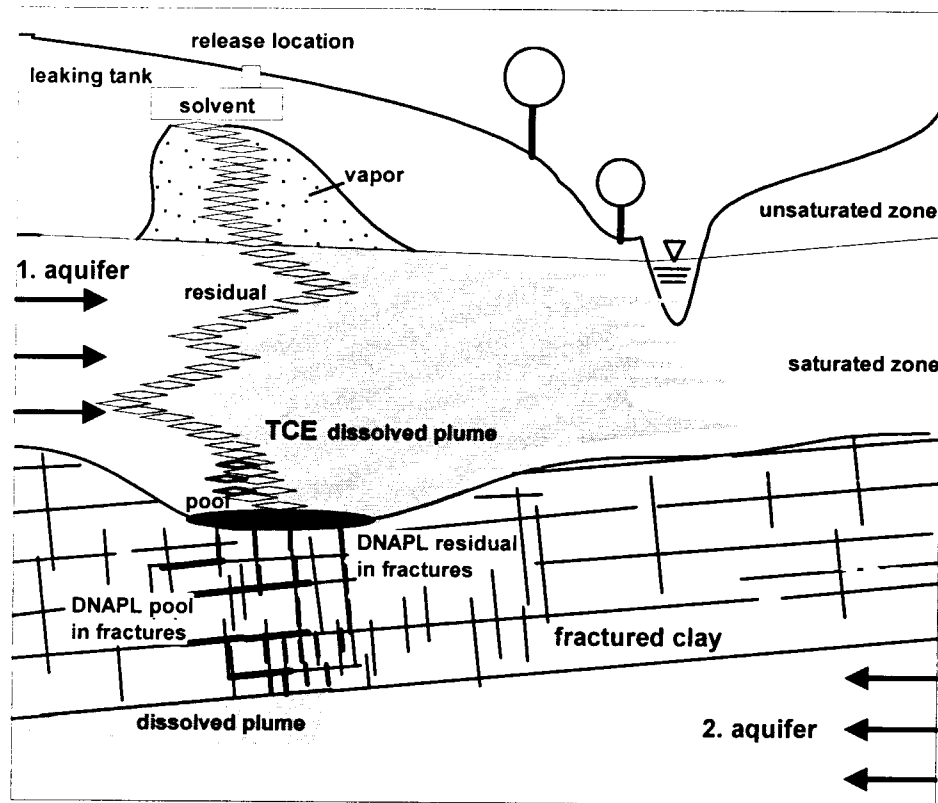

Figure 1: Behavior of DNAPLs in an aquifer; the existence of a clay horizon must not guarantee an absolute protection for the underlaying aquifer.

Because the DNAPLs undergo physico-chemical reactions while being transported through an aquifer, their movement rate may be less than the average groundwater flow rate. Such reactions that slow movement of contaminants in an aquifer include under other things adsorption and partitioning into organic matters or organic solvents.

Also, the transport of DNAPLs is controlled by complex interactions between biological processes and the contaminants, the result may be a microbiological degradation. Most of the DNAPLs degrade in the natural environment faster when anaerobic conditions exist. The resulting intermediate (not completely degraded) products are often undesirable and more hazardous than the parent compounds and more or less stable and mobile in the underground.

3 Site investigation strategies and collection of soil, soil gas and groundwater samples

Remediation of contaminated groundwater has as basic requirement the investigation and a following assessment of the groundwater quality.

Between investigation, assessment and remediation there exist relationships. In the case of not understanding, many field investigations become both inadequate and costly. An unsufficient investigation is a source of error in respect to risk assessment and often has as consequence the total failure of remediation efforts. We can say: "The investigation with its site-specific requirements of collection and interpretation of the data is very often the weakpoint of the remediation"!

- <u>procedure steps</u>

At different times in the life of an investigation project, a lot of information will be required. Although each investigation is unique, there are general rules. Regardless of the complexity or detail of the investigation, a logical series of steps should be followed. Each step has to be checked up in respect to its efficiency; if necessary, the initial goals should be reviewed. Besides of the urgent or emergency measures, the hierarchically staggered phases of the investigation program are: inventory (or initial resp. preliminary investigation), standard investigation, main or detailed investigation and, if necessary, also special researches (fig. 2).

At the begin of the investigation, normally the data-gathering activity is focused on the determination of whether or not contamination of soil and/or groundwater exists. Based mostly on existing records the inventory includes an preliminary assessment in respect to the localization of the spill sites (history), the reasons of contamination and the responsibility for the calamity, as financial aspects are important, the geological and hydrogeological conditions, surface waters, and sewerage systems.

Later, after the contamination has been verified, the focus of the investigation shifts to the contamination areas in the underground as well as to the proof and configuration of the plumes perhaps in several aquifers.

Still later, before the remediation can begin, the investigation is focused on the definitive evaluation of the environmental damage and also on the data acquisition to determine the remediation technologies adaptable to the site-specific contamination problems. The more qualified the investigation is, the better and easier the choice of remediation methods will be.

Often the investigator must repeat some of the initial work with a specialized purpose. However, if the initial data gathering is sufficiently detailed, the second effort will be less repetitive, more effective, and less costly.

One of the easiest ways to insure a successful outcome is to prepare a detailed written site-explorative program, combined with a checklist (table 5). For instance, a listing of underground storage tanks should identify the presence of otherwise hidden potential sources which may be contributing contamination.

Because of the lot of problems to be solved and the interdisciplinary character of the investigation and remediation, a working group with focal point character, information multiplier, and decision making function should be established.
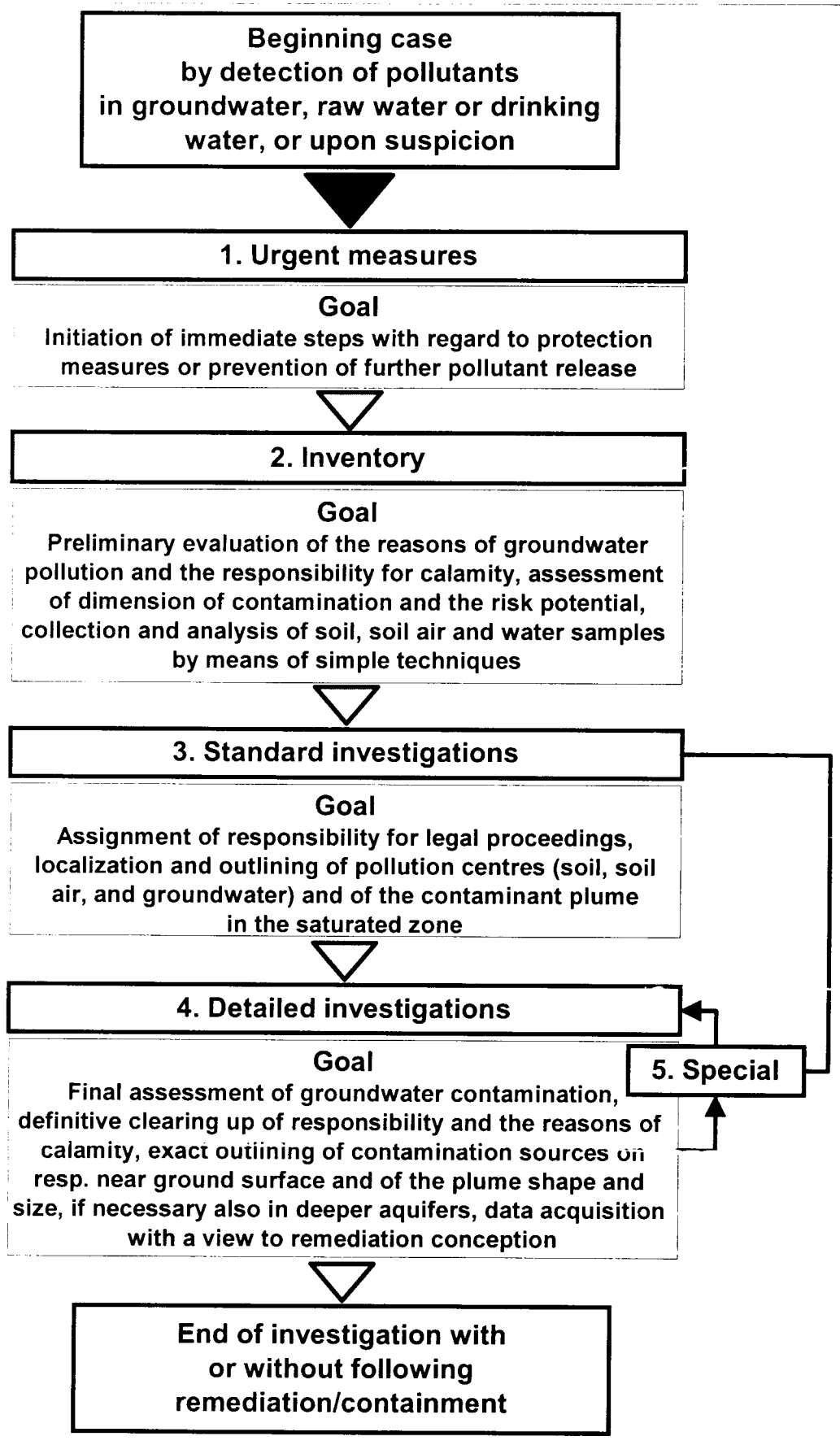
Figure 2: Schematical sketch of investigation steps.

Table 5:   Checklist for standard and detailed investigations

- Complete description of physical characteristics of the site
  - maps, diagrams, charts describing the site and its surroundings
  - topographic mapping of the site showing infrastructure (utility lines, e.g installations of storm or sanitary sewers, streets, city roads, buildings etc.)
  - drawings showing the location of the contamination sources (underground tanks, sewers, other buried lines and utilities, ramp, storeroom for solvents, distillation plant, waste water treatment plant etc.)
  - location of other potential sources of contamination in the vicinity which may be contributing to the site contamination
  - location of public/ private supply wells and monitoring wells

- Description of site geology/hydrogeology
  - complete description of regional and local geology
  - maps and geologic fence diagrams showing location of borings, and the depth and type of formations
  - maps and diagrams showing the hydrogeology at the site
  - a description of the groundwater quality incl. a summary of chemical data
  - maps and fence diagrams showing the extent of the contamination in soil and groundwater
  - maps showing the areal extent of the contamination in the vadose and the saturated zones

- Description of the site (geo)hydrology
  - principal description of the regional (geo)hydrology and water budget for the site
  - determination of the hydraulic conductivity and storage coefficient for each of the relevant aquifers as determined by pumping or hydraulic borehole tests
  - description of the direction of movement and rate of field velocity in each relevant aquifer
  - rate of movement of the contaminants in each relevant aquifer
  - maps showing the equipotential flow lines for each relevant contaminant zone and aquifer (different fixed days)

- Chemical characteristics and treatability investigations
  - summary of chemical and physical characteristics of the soils
  - description of soil and water treatment alternatives
  - projected time required for cleanup under different alternative remediation methods
  - projected total costs for maintenance, sampling, and operation for each treatment system and cleanup alternative
  - permits required to operate and maintain the treatment system, and types of operators required for proper operation
  - estimated costs of engineering, construction and installation for the systems under consideration
  - description and rational selection of the preferred method of treatment, including calculations and preliminary design sketches
  - recommended alternative for the treatment of the contamination problem
  - discussion of any public health impacts or problems from operation of the treatment system

- <u>sampling methods - possibilities and limitations</u>

As the decision to investigate and to clean up is governed by the analytical values obtained, it is absolutely necessary that the results obtained must give a correct insight into the real in-situ distribution of the pollutants in the underground.

In the reality, very often the in-situ contamination is not reflected in the measured values, the concentrations and the pattern of the pollutants in question may be in error by orders of magnitude. The real cause of inaccuracies in concentration results lies mostly not in the laboratories, but in a high degree in the not proper and not site-adapted sampling techniques. Another weakpoints are the steps preceeding like taking in account the hydrogeologic characteristics of the site, the correct planning of monitoring network, the installation of observation wells etc. A good consultant resp. investigator with long-term experience knows and has the possibilities to minimize the faults and weakpoints of sampling methods (fig. 3).

Following, there is given a guidance on sampling procedures, referred to the several phases of the DNAPLs.
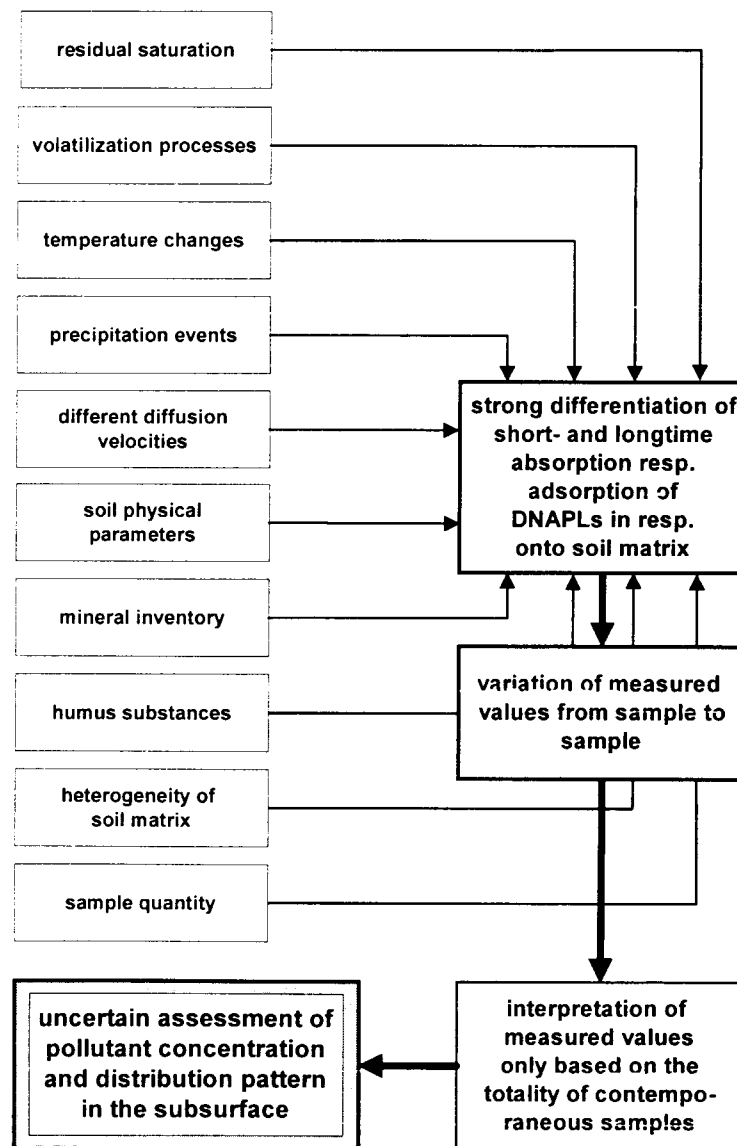

Figure 3:   Influences on the DNAPL concentrations especially in soil and soil air samples.

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– Soil sampling

Soil samples are taken from boreholes or excavations. Most of the soil sampling is done in the unsaturated zone. Often the intent of soil sampling is to determine the volume of polluted material for excavation or air stripping (see later) and its degree of contamination. The information gained also helps in estimating actual and future groundwater pollution by the contaminated soil.

Soil samples from excavations are usually taken by Shelby tubes pushed into the walls. An advantage of excavations can be the view of the near-surface geology, but the high costs for excavating often prove to be a serious disadvantage. This method may also not be applicable underneath or near buildings. Furthermore, the conditions at sampling time are not representative for the subsurface situation before the opening of the excavation. There are losses caused by changes in temperature and by dissolution of DNAPLs in precipitation water hitting the walls of the excavation. Samples

Only drilling techniques without circulation of air, water or mud can be applied without loss of volatile pollutants from the sample. In connection with an environmental contamination, soil samples are generally taken with small diameter (1'' or 2'') sounding drills which usually are rammed into the ground by motor driven hammers.

This low cost and high speed method has grave disadvantages. Compression of core material often disturbs the geologic log and makes an exact depth determination difficult. Within the drillstem, polluted material may spread significantly beyond its original position leading to cross contamination within the borehole. The small volume of the samples encourages losses by degassing due to its unfavourable ratio between volume and surface area. Vibration effects can cause separation of liquid phase and matrix and lead to subsequent migration and loss.

In total, soil sampling by ram sounding drills only provides qualitative results. In regard to quantity of pollution the results could be completely unreliable, for the above reasons.

Best drilling results are obtained with a method similar to split-spoon sampling. The core barrel used is lined with PVC or teflon. Its length is 0.5 to 3 m with an inner diameter of up to 10 cm. After drawing of the drillstem, the PVC or teflon pipe is immediately sealed at both ends. It is then delivered to the laboratory in its entirety. The disadvantage of this method is the high cost.

In the laboratory, analytical work should only be done with the inner part of the sample, because in the outer fringes degassing losses and adsorption effects onto surfaces can be significant.

Soil sampling returns only point values for contamination, due to the very often small-scale heterogeneity and permeability variations of the soil volume. Matrix heterogeneities of the soil (fig. 4), as well as climate (air pressure, temperature, precipitation) dependent changes in the dynamic equilibrium between organic molecules and the surface forces of the matrix particles of the soil make spatial and time related concentration variations within the soil unpredictable. Detailed knowledge of the local geology helps, however, in estimating the true conditions. Therefore, it is important to take depth-dependent samples in accordance with the geological profile (fig. 5). Because of the point character of the values, it is not meaningful, first to present the pollutant contents in iso-concentration lines and second to do this without relation to the soil properties, for example grain size.
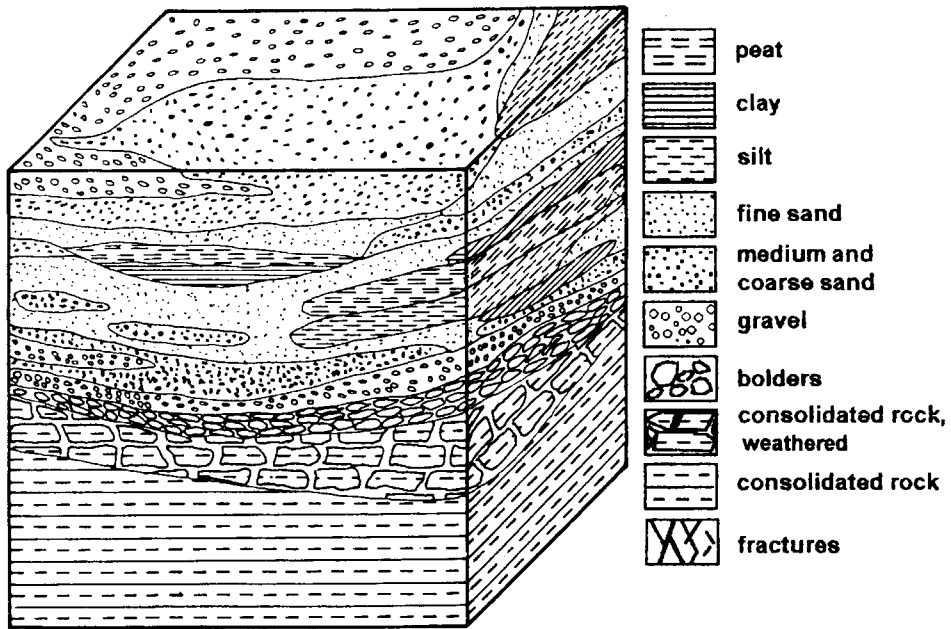
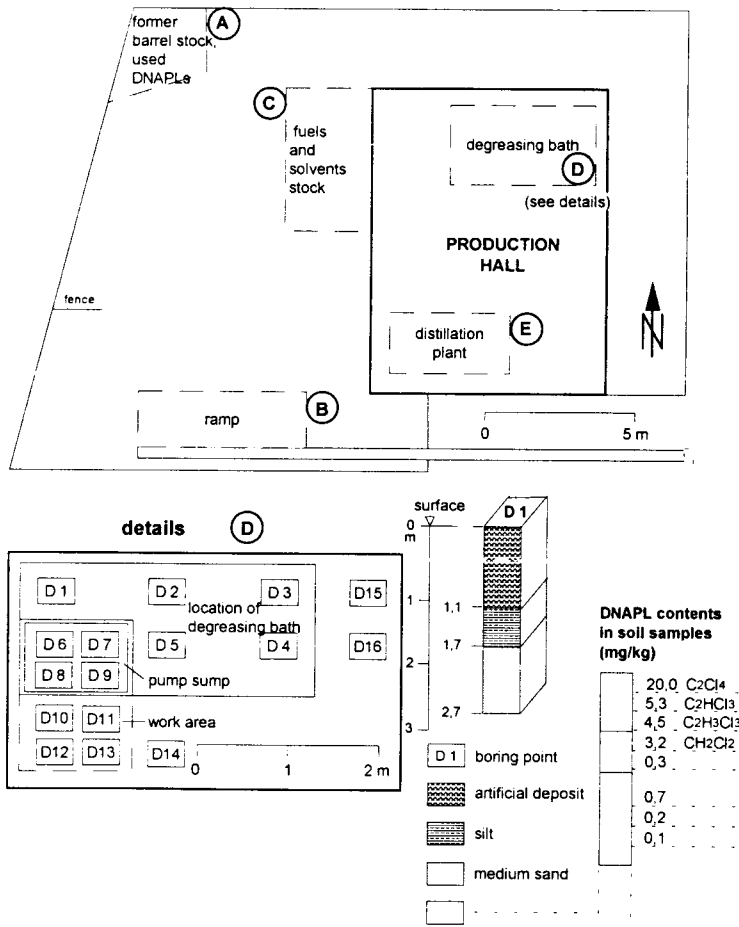Figure 4:   Schematic block diagram of unconsolidated and consolidated rocks

Figure 5   Example for presentation of DNAPL contents in soil samples.

– Soil gas sampling

Low costs make soil gas sampling an attractive investigation method. The method is seemingly simple and results are obtained quickly. A variety of methods exists, all of them use the flux of pollutants, mostly by diffusion, into the soil air which is captured for concentration measurements. Boiling point and vapour pressure determine the flux of the pollutants from soil or groundwater pollution into the soil air.

This flow of polluted air is captured for concentration measurements by gas chromatography analysis or by testing tubes (a colour indicator in the tip of a tube gives the approximate degree of contamination, integrating several species of contaminants).

Active sampling by a syringe (direct injection method) or by a piston pump (enrichment method, injection of eluate) is preferred. Also there is long-term passive sampling with in-situ adsorbing of DNAPLs from soil gas onto buried activated carbon or resin.

Singular samples are not of great value. A large number of samples is necessary for a meaningful interpretation, because the small volumes taken (sampling by syringe typically captures some cubic centimeters, by piston pump about 20 litres of soil gas) reflect only local conditions.

Depth profiling of soil gas pollution helps to identify the type of pollution sources involved. Depth profiling can be achieved by installation of separate boreholes to different depth (fig. 6) or by analysis of air from core samples. Packer systems are difficult to install and unreliable because of the small diameter of boreholes.
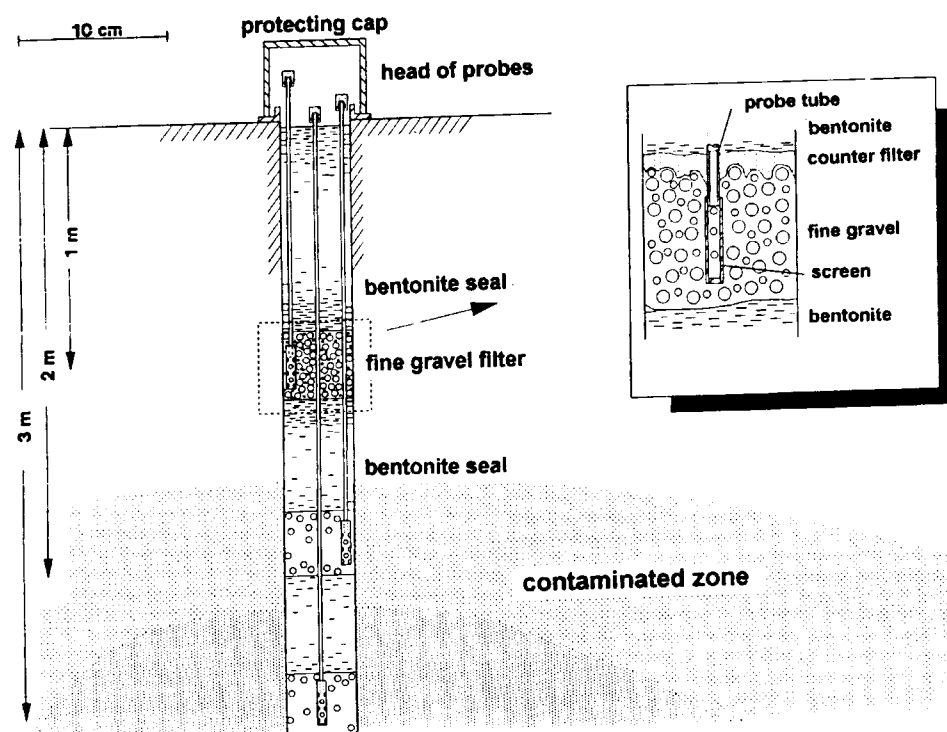

Figure 6: Sketch of a stationary soil air sampling point (probes in three different depth levels).

The shape of concentration-versus-depth curve helps separating sources within the vadose zone from sources within the saturated domain (fig. 7).

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Existing sources in the unsaturated zone would show up with peaks along the vertical sampling line. This would be the case for pollution from sewers, underground storage tanks etc.

Should degassing of unconfined groundwater be the source of soil gas contamination, then concentrations would increase with depth. Here, the shape of the concentration-versus-depth curve is mainly determined by two parameters: 1) reduction of concentration caused by diffusive or advective processes and trapping of volatiles by soil moisture, and 2) the effects of geologic and lithologic pattern in the unsaturated zone. These processes determine the type of modification of the simple concentration curve, for instance under an sealing surface layer or a series of partially inhibiting lenses. The chance of detecting of pollution within a confined aquifer in the soil gas of the overlying unsaturated zone is practically non-existent.

In humid climates the distance between the groundwater table and sampling points should not exceed 20 to 25 m, and highly permeable layers, such as sand and gravel, should prevail. Low-permeability material and high water content in the unsaturated zone tend to inhibit the migration of gas.
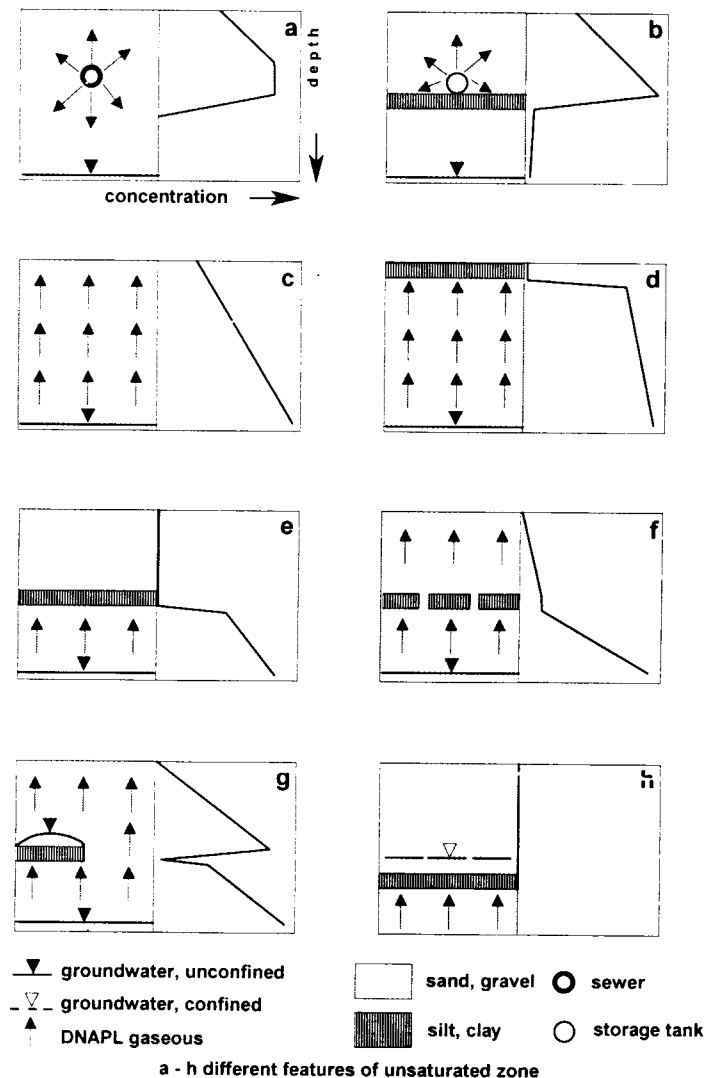

Figure 7: Concentration of soil gas in dependence of hydrogeology and source of pollution (left half: hydrogeology; right half: concentration of DNAPLs);
c – h: concentration of soil gas over polluted groundwater plume under differing geologic and hydrodynamic conditions (unconfined: c – g, f; confined: h)
a, b: effect of a source of pollution in the unsaturated zone.

Besides the above mentioned problems with sampling methods, representativeness of samples, analysis techniques, and the effect of geologic conditions, several additional disadvantages have become known. Cable, pipe and conduit installations enhance degassing processes and may lead the soil gas far away from the source. Similar processes are at work beneath paved areas and buildings. These processes tend to give misleading information with respect to the location of the pollution source. Sealing of the surface by any means collects and thereby increases the concentrations.
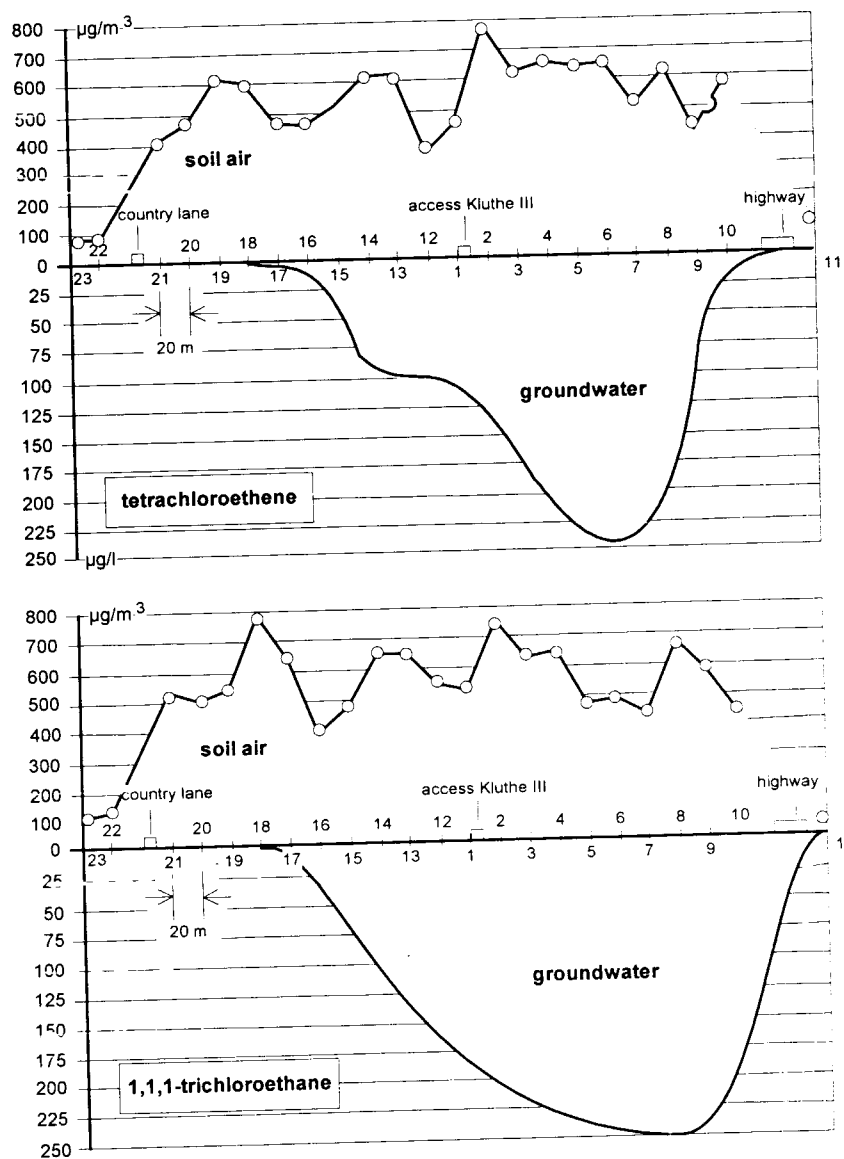

Figure 8: DNAPLs concentrations in soil air in comparison with groundwater – groundwater deterioration Heidelberg/Germany.

Sample series taken in the same area at different times cannot be readily compared and are often impossible to interpret. Precipitations cause lower concentration values in soil air as increasing water content within the pore space reduces the liquid and volatile DNAPLs. Low temperature and especially freezing of soil tend to drap volatile DNAPLs by condensation.

Nevertheless, soil gas sampling can deliver valuable insights into subsurface pollution. It is suited to detect the centres of soil contamination (fig. 8) and to optimize the selection of monitoring wells when supplemented with proper drilling and groundwater sampling programs. It does, however, not replace groundwater investigations.

– Groundwater sampling

The results of the direct measurements of groundwater chemistry are the best ones, they determine the human health risk and the need for remediation.

In a first step one might want to make use of previously installed water supply wells and water table observation pipes. In general, both is not adequate for sampling DNAPLs. Large diameter or suction-lift well arrangements encourage significant degassing. Monitoring wells with very shallow or very deep screen positions often miss the pollution plume. Wells and observation installations with screens in two or more aquifers are totally inadequate. They cause cross-contamination between aquifers and must not be used for sampling. Also, they do not allow any meaningful measurements of potentials needed for the determination of flow directions.

Groundwater flow systems require depth-dependent monitoring and sampling (fig. 9). Screen positions need to be well selected within an aquifer with heterogeneous permeability. Screening the total length of a thick aquifer is not good practice, not even for a first assessment of the presence of contamination. Installation of a fully screened pipe often changes the flow field of an aquifer significantly.
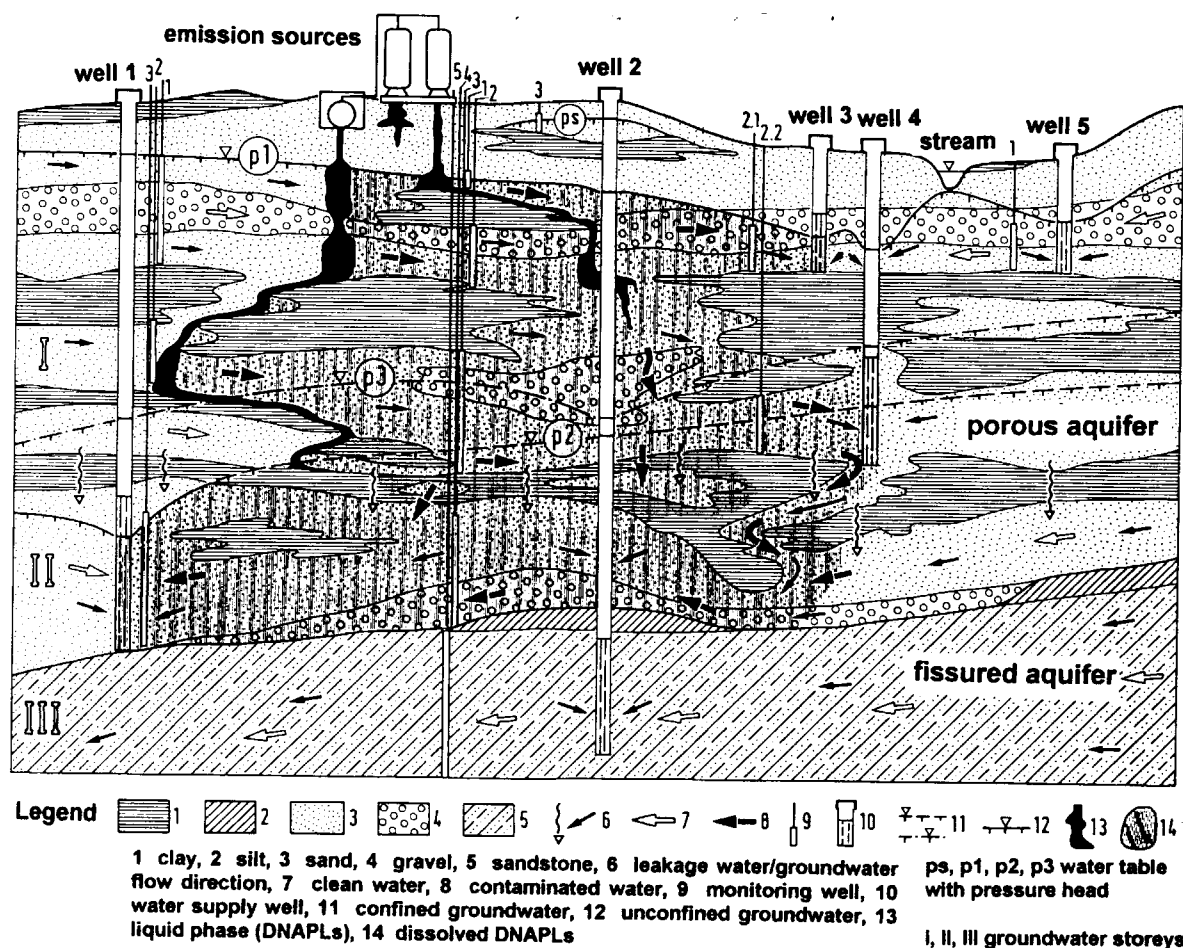

Figure 9: Three-dimension groundwater investigation.

Packer systems are often used, in order to obtain level-accurate samples from wells with long screens. However, numerical simulation shows the possible errors resulting by using packer systems. The main problem is the geology; layers with a higher hydraulic conductivity deliver

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better results resp. have more representative samples as consequene than less permeable formations, which are very often much more strongly contaminated.

The material of the monitoring wells and the sampling equipment can adsorb DNAPLs. Therefore, the contact time between water and PVC should be minimized by longtime pumping such that adsorption effects are negligible. It is known also, that dissolved DNAPLs at saturation concentration can destruct PVC casings. That means, that monitoring wells situated in a contaminant source should consist of stainless steel or teflon.

In regard to the sampling itself it is the general view that pumping is better than bailing. Only in the case of organic liquid phase, either floating near the groundwater table or collected in pools on the top of an impermeable layer, bailing can be the better alternative.

Pumping should only be done with submersible pumps or other pressure increasing systems, not with suction pumps. Use of suction pumps would enhance degassing of water.

In a homogeneous and in a multi-layer-aquifer equal pumping can have very different influences. In the case of pumping at the top of a two-layer aquifer in which the upper layer with the lower hydraulic conductivity is relatively thin but highly contaminated, the resulting concentration can be considerably higher than the real flux-averaged concentration. Pumping at the bottom of the two-layer aquifer also causes an underestimation of the pollutant concentration due to the inflow velocity distribution resulting in this case. This means that the position of the pump intake in layered aquifers has a greater influence on the resulting values of the pollutant concentration than in homogeneous aquifers.

Finally, sampling requires careful handling of the water itself. It should be placed into the sample container without turbulence and in such a manner that degassing is prevented as much as possible. 10 or 20 cm³ glass bottles with headspace and teflon septum are often used as sample containers. Air from the headspace is then analysed and the results are back calculated for pollutant concentrations in water, using partition coefficients for water/air systems. The accuracy of this method has been found superior to others.

4 Case histories in the region of Frankfurt/Hesse/Germany

Three examples will be discussed, located in the surroundings of Frankfurt (fig. 10): the groundwater contaminations at the Frankfurt Airport south of Frankfurt (porous aquifer), at City of Dreieich southeast of Frankfurt (consolidated rocks) and at City of Hadamar northwest of Frankfurt (karstic rocks).

In view of hydrogeological settings, contaminants and pollution causes, the three Hessian case histories are not unique, therefore, conclusions from the activities and results, documented in the tables 6, 7 and 8, in view of the situation in the ESCWA countries are possible. The intention of the author is to present some of the difficulties faced in practical work and to document weakpoints and pitfalls, thus helping for learning.

The remediation technologies refer to conventional withdrawal and cleaning of groundwater (pump-and-treat) and suction and cleanup of soil air.
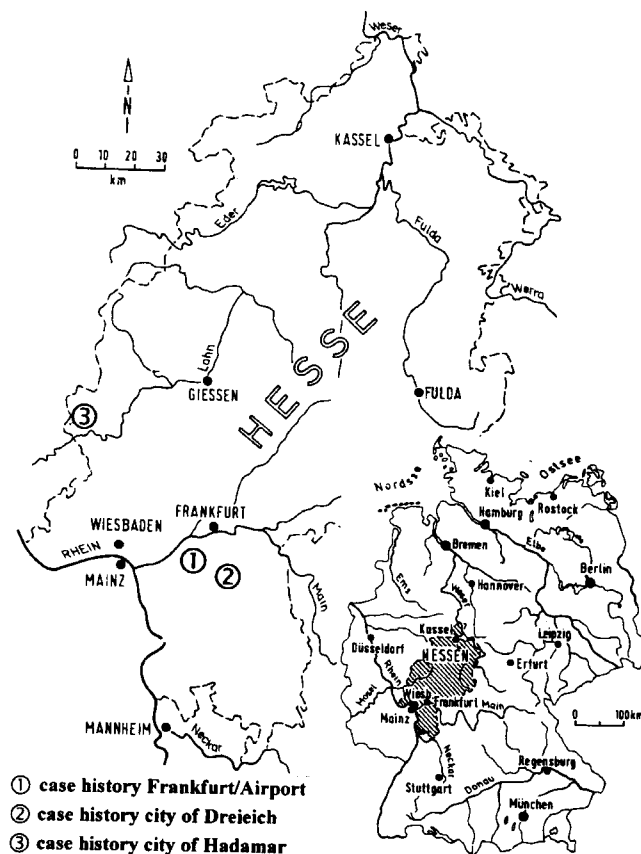
Figure 10: Location of Hessian case histories discussed in detail.

- Frankfurt Airport

– History and geology

Contaminants are mainly tetrachloroethene, trichloroethene, and also 1,1,1-trichloroethane. Cis 1,2-dichloroethene occurs as an intermediate product of biodegradation, a so-called metabolite, especially in the front part of the plume.

The contamination was recognized in 1977 when organic compounds were found in drinking water from wells of one of the water works of the City of Frankfurt, located in northern direction about 300 m away from the airport.

The airport opened in 1936 and first contamination may have started at the end of the sixties with the beginning handling with the solvents. The amount of contamination could well exceed 100 tons of DNAPLs.

Sources were the sewer discharge from the hangar of the Lufthansa airline, a car repair shop, a storage area for barrels with solvents, an underground storage tank for solvents, careless handling of solvents in the parking area for airplanes, and a testing facility for airplane engines.

The subsurface consists of 30 to 50 m of coarse sand and gravel of the Quarternary underlain by 110 to 140 m of fine to medium sand of the Pliocene. The hydraulic conductivity of the upper aquifer is between 10^{-3} and 10^{-5} m/s and that of the lower aquifer probably between 10^{-3} and 10^{-7} m/s. Between the two aquifers, a dividing layer of silt and clay exists in places. The lower aquifer is underlain by more than 100 m of silt and clay of the Miocene. The groundwater flows in NW direction with a field velocity of 0.5 - 0.6 m/d. The depth to its table is 12 to 15 m.

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– Investigations

In 1978 groundwater and soil gas investigations were started and were finished in the year 1990 (besides of later control measurements). Groundwater investigation was first done by using about 25 existing wells and monitoring wells. Construction details were often not known. From 1978 to 1989 in total 43 monitoring wells of 4'' to 6'' diameter dedicated especially for sampling were installed step by step with the goal to determine the location of the front and the shape of the pollution plume. In 1988 and 1989, 25 additional monitoring wells of 2'' diameter were installed near four remediation wells. These monitoring wells are only for hydraulic observation.

Within the plume, dissolved concentrations close to the source were originally about 80 mg/l. Today it is about 2 mg/l and less because of active remediation and potentially as consequence of activities to divert the plume hydraulically by infiltration of water. Sometimes the concentrations are higher again; one can suggest, that liquid phase was mobilized, the reasons are unknown. Along the centre line of today's plume concentration values range from about 1 mg/l about 1 km downstream of the source to about 0.1 mg/l close to the front.

By now the plume is about 3.5 km long and 850 m wide within the upper aquifer (fig. 11). Some pollution in the µg/l range has reached the lower aquifer.

In its course the plume passed through a field of six industrial pumping wells. Four of them were screened in the upper and lower aquifer and therefore their cones of depression have not only an unsufficient function as a hydraulic trap, but, furthermore, they favour the leakage of dissolved DNAPLs into the second aquifer.

Basing on some sampling results it cannot totally be excluded that the plume in the upper aquifer might have migrated under the nearby River Main to the other side. This would indicate that the River Main may not function as a hydraulic barrier and recipient of groundwater flow. The reasons might be that the nearby dam step causes the accumulation of fine materials which colmate the river bed and thus interrupt the hydraulic contact between surface water and groundwater.

Some 495 samples of soil gas were taken over the length of the investigation period in blocks (table 6). Sampling and analyses were often done by different consultants and laboratories at differing sampling sites. Accordingly, results for the different sampling events cannot meaningfully be compared.

Soil gas sampling was intended to outline the areas of source pollution in soil and the plume of contamination in groundwater. Concentration values in soil gas were between 3.7 g/m^3 near the source areas to some mg/m^3 over the polluted groundwater about 500 m downstream of the sources.

The distribution of soil gas concentrations along sampling lines disagrees somewhat with the interpretation of groundwater data. Soil gas values are documented in the small shaded curve areas in figure 11. Immediately apparent are disagreements just south of the source area and west of the plume. The reasons for the peaks are not known. It appears, however, that additional unknown sources of pollution may exist south of the area discussed. The lack of high values of groundwater pollution in this area may be caused by clay layers in the unsaturated zone protecting the groundwater from contamination from above.
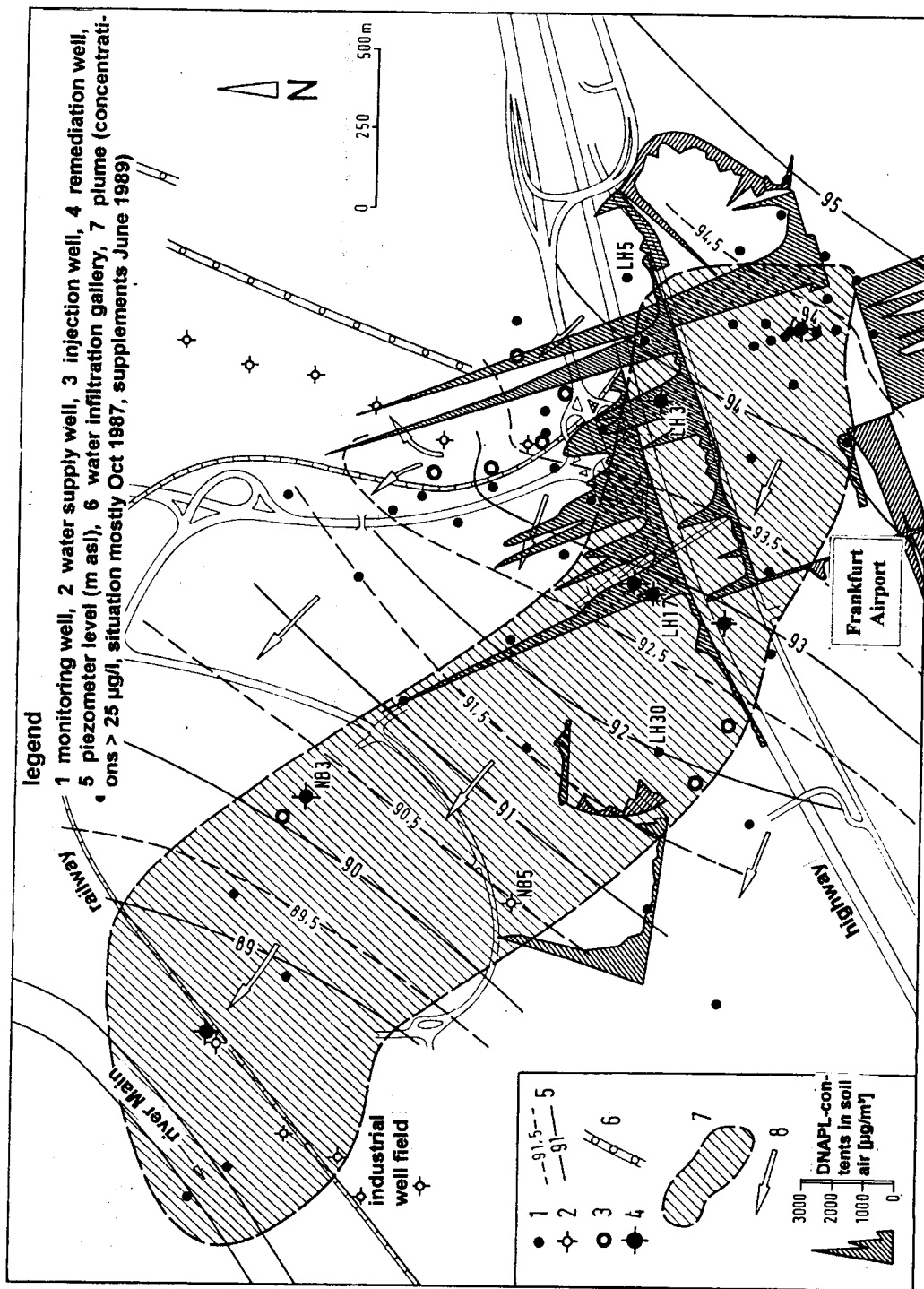
Figure 11: Plume of dissolved DNAPLs and associated soil gas concentrations.

- Remediation

Of immediate concern in 1978 was the protection of existing water supply wells about 300 to 500 m north of the pollution sources. The southernmost of the wells was abandoned in 1978. Additionally to artificial groundwater replenisment with cleaned water of the River Main since 1959, five water injection wells were installed 1981 to the south and southwest of the line of water supply wells to hydraulically divert the moving plume of pollutants to the west. The operation was successful, but contrary to all exspectations and targets, no dilution took place, only the plume was pushed aside. Therefore the pollution spread to a groundwater area, that wasn't yet touched until then (fig. 12).

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Remediation of the pollution areas have been undertaken since 1983 with groundwater pumping (10 - 20 m³/h) in one well situated nearby the formerly leaky sewage canal. This well evacuated about 3,114 kg of solved DNAPLs between April 1983 and March 1995. Since September 1988 three additional wells were operated in the lower half of the plume in order to decontaminate the groundwater used by a chemical factory. In September 1988, March 1991 and March 1995 three wells started pumping in a line across the plume at the northern boundary of the airport. All these wells produced about 4,584 kg of solved DNAPLs until December 1998. Considering about 250 kg of DNAPLs collected additionally since summer 1997 in connection with the deep foundation of a railway tunnel crossing the contaminant plume, the total hydraulic removal amount of DNAPLs was 7,947 kg so far. The almost DNAPL-free water treated in five plants is disposed of to sewers.

In situ soil decontamination by air stripping was started in September 1989 with three suction wells distributed over three of five pollution centres within the unsaturated zone. The screens of the suction wells were positioned in the centre of soil gas pollution. The amount of DNAPLs extracted was about 1375 kg until 1998 (the last report of the consultant refers to this year).
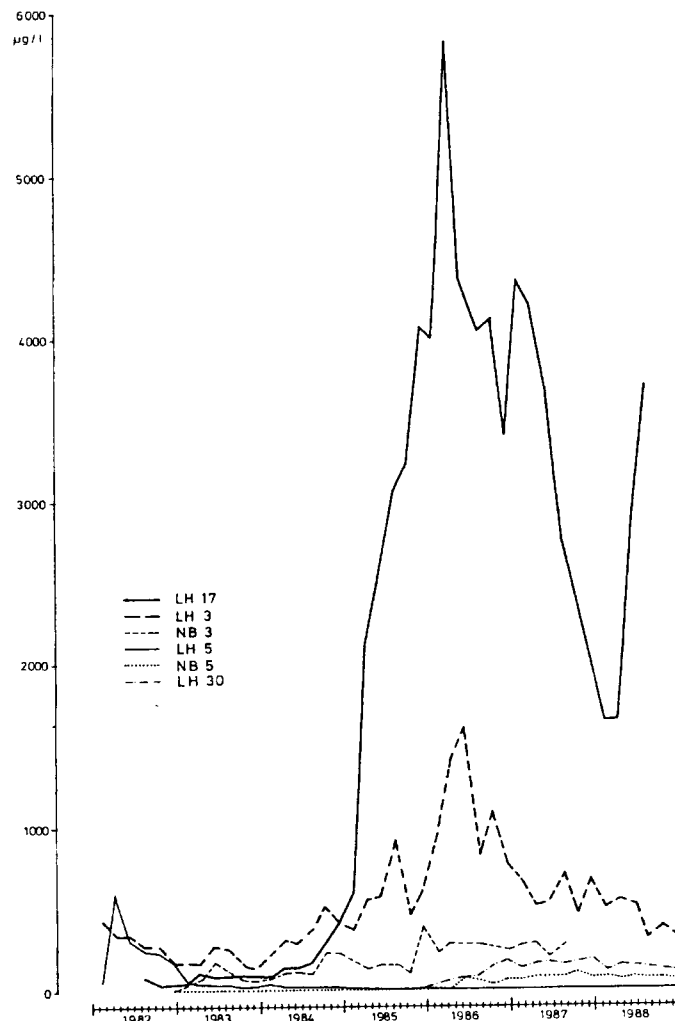

Figure 12: Diversion of the moving plume to the west caused by water infiltration (hydraulic containment technology).

Table 6: Synoptic summary of subsurface pollution by DNAPLs at the Frankfurt Airport

CASE	Frankfurt Airport
Case	Frankfurt Airport unconsolidated rocks major German airline
Sources of contamination	sewage canal in airplane repair facility, car repair facility, storage of barrels and underground tank with solvents, test facility for airplane engines
Type of DNAPLs	tetrachloroethene, trichloroethene, 1,1,1-trichloroethane; cis 1,2-dichloroethene as metabolite
Start of leakage	possibly at the end of the 1960s
Geology/Hydrogeology	upper aquifer: 35 - 50 m coarse sand and gravel (Quarternary); lower aquifer: 110 - 140 m fine and medium sand with silt and clay lenses (Tertiary); dividing layer: 5 m silt and clay with windows (Tertiary)
Depth to water table	10 - 15 m
Coefficient of permeability	upper aquifer: 10^{-3} - 10^{-5} m/s; lower aquifer: 10^{-4} - 10^{-6} m/s; (from pump tests at water wells)
Field velocity of groundwater	0.5 - 0,6 m/d in upper aquifer
Type of investigation	soil gas: 495 samples; groundwater: 43 monitoring wells installed
Degree of pollution	soil: not measured; soil gas: max. 3.7 g/m^3; groundwater: max. 80 mg/l
Spread of pollution - liquid phase	not known
- plume	upper aquifer: length 3.5 km, width 0.8 km, thickness 30 - 40 m; lower aquifer: not known
Remediation	injection of cleaned river water since 1981 to divert plume; withdrawal and cleaning of groundwater in steps since 1983; suction and clean up of soil gas in steps since 1989

So far, the amount of payments made for investigation and remediation exceeds about US$ 40 million. The total amount of DNAPLs extracted by remediation has been totaly 9.3 tons. That means that the price for 1 kg tetrachloroethene is very, very high, namely about US$ 4,300; in a chemical store, one would pay for the same amount only US$ 0.7. Therefore the message is, that the prevention of a calamity by means of high technology and carefullness is often much less expensive than environment-related repair measures.

– Comments

It appears that the investigation was not done with as much vigor as one may have expected. No investigation has been done to illuminate the fate of liquid phase and, thus, no removal of soil with the immobile liquid phase in the source areas has been started. Even today the exact configuration of the plume of contamination is not known.

A general strategy for the groundwater investigation is still missing. At no time was there an educated attempt made to understand all the implications of the case. At the source, clean-up efforts have been insufficient and were started too late. The same applies for the plume. At one time it was thought that injections at the water well site would also reduce the pollutants' concentration by mixing. Since January 1990 it cannot be excluded that a number of Frankfurt water supply wells north of the River Main might be threatened by the moving plume. The hydrodynamics of groundwater flow in the area were not understood adequately, most of the members of a former working group did not see the problem so seriously.

The special message is, that an not enough site-related investigation of a groundwater contamination makes the following remediation measures very expensive and ineffective. Despite of pumping over almost 20 years the size and shape of the contaminant plume remain unchanged, only the DNAPL concentrations in the groundwater have been decreasing slowly.

- City of Dreieich

– History and geology

A precautionary investigation of a medical needle factory by a regulatory agency in 1986 indicated that contamination by DNAPLs could have occured in two areas. The courtyard held a storage area with barrels containing used and distilled solvents, without any protection against seepage into the subsurface. In the basement, the solvent distillation and recycling plant had a capture basin for leakage made of concrete only, without a protective coating. A first investigation of the soil gas under the two suspected source areas revealed pollution values of up to 5.7 g/m^3. A detailed investigation was then ordered by the regulatory agency. In 1988 a third source area was located, caused by collection of heavy DNAPL vapours at the deepest point of the basement and subsequent seepage of DNAPLs through the concrete floor into the soil by gravity flow.

Estimates of the amount of solvent leakage into the ground are difficult because of the unknown, but certainly significant degree of volatilization. After refit of the distillation and recycling plants, the need for replenishment of DNAPLs was reduced dramatically to less than 20 %. From that one may conclude that tons of solvents must have seeped into the subsurface.

Built in 1965, the factory is located on soil above fractured red beds consisting of claystone, siltstone, sandstone, conglomerates, marl, and non-karstic limestone (fig. 13). Intrusions of basalt and diorite are present close by. The upper 4 – 5 m of rocks are weathered.

Hydraulic conductivities for the different rocks are not known at that site. The pattern of jointing and faulting also has not been investigated. The nearby positioned edge of the Rhine graben rift suggests occurrence of SW-NE faulting parallel to the edge of the graben at that location. The slope of the groundwater table is to the NW. Over fractured rocks it occurs at 3 to 4 m depth, at the edge of the graben in porous media it is said to drop to 17 m. Permeability of the Permian formation is unknown, but seemingly very low.

– Investigations

In 1987 holes 1,2 and 3 were drilled for the investigation and instrumented with monitoring wells. Holes 4 to 8 were drilled independently in 1988 by another consultant for a different client during investigation before purchase of a property. They were abandoned and sealed after one-time sampling of groundwater in open holes. Holes 10, 11, 13, and 14 were drilled in 1989 for the factory by the previous consultant. Holes 9, 12, 15, 16, and 17 are wells existing since decades. Only some technical data are known for these holes. The regulatory agency has installed four monitoring wells upgradient from the factory area, and another polluter nearby (C in fig. 13) further four wells.
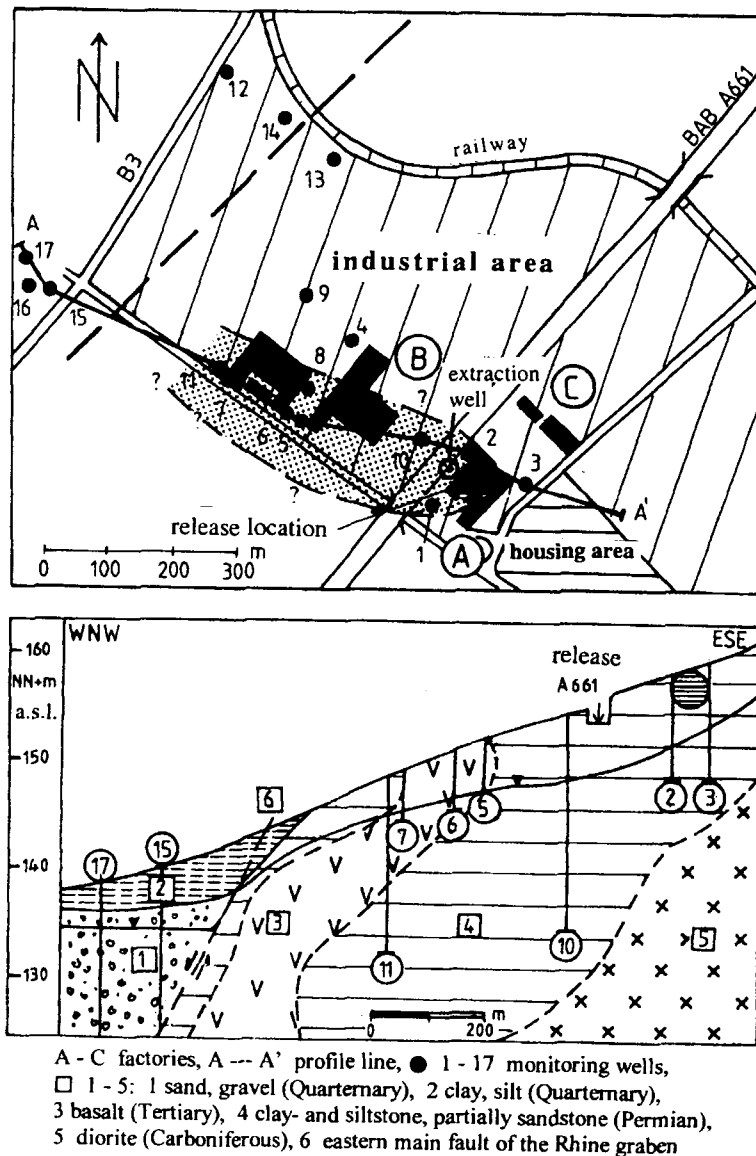
A - C factories, A — A' profile line, ● 1 - 17 monitoring wells,
□ 1 - 5: 1 sand, gravel (Quartemary), 2 clay, silt (Quartemary),
3 basalt (Tertiary), 4 clay- and siltstone, partially sandstone (Permian),
5 diorite (Carboniferous), 6 eastern main fault of the Rhine graben

Figure 13: Migration of dissolved DNAPLs in consolidated, fractured rocks, City of Drei-
eich. Upper part: birds eye view, lower part: cross-section.

Contamination in groundwater was found to be between not detectable and 41 mg/l (table 7).
The spatial distribution of the values suggests a complex pattern of migration. Considering the
components of the contamination at the different boreholes, the picture becomes even more
confusing. Just down-gradient from the needle factory monitoring wells 2 and 3 show predo-
minance of tetrachloroethene over trichloroethene in a ratio of 80 to 20. Monitoring well 3,
technically just groundwater up-gradient from the factory, shows predominance of trichloro-
ethene over tetrachloroethene in the same ratio. The factory claims to use no trichloroethene at
all.

Most of the other holes show a slight predominance of tetrachloroethene over trichloroethene.
Hole 13 has a very strong predominance of 1,1,1-trichloroethane. The source of this substance
was an abandoned landfill nearby, now remediated.

The contaminant plume, potentially caused by several companies and therefore beginning at
different sources, has obviously entered in the porous aquifer of the Upper Rhine graben.

A line of soil gas sampling points was put across the suspected contaminant plume down-gra-
dient from the factory with 10 boreholes sampled in 1987. The maximum contaminant content

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of about 1 mg/m^3 was unexpectedly found at the southwestern end of the sampling line with tetrachloroethene dominating. The concentration in all other holes was only the background value for soil air of about 200 μg/m^3 Hence the results of this investigation increased the confusion.

Table 7:   Synoptic summary of subsurface pollution by DNAPLs at the city of Dreieich

CASE	City of Dreieich
Case	City of Dreieich consolidated, fractured rocks plant for medical equipment.
Sources of contamination	barrel storage area for solvents, solvent recycling process (distillation)
Type of DNAPLs	tetrachloroethene, trichloroethene, cis 1,2-dichloroethene
Start of leakage	possibly since 1965
Geology/Hydrogeology	sequence of sandstone, siltstone, conglomerates and thin, non-karstic limestone layers (Permian) with intrusions of diorite and basalt (Tertiary); located at the edge of of the Upper Rhine graben
Depth to water table	3 - 5 m
Coefficient of permeability	not known
Field velocity of groundwater	not known
Type of investigation	soil: 1 cored borehole soil gas: 10 samples groundwater: 8 monitoring wells installed (and other 8 monitoring wells installed by regulatory agency and another polluter)
Degree of pollution	soil: max. 2.6 g/kg soil gas: max. 5.7 g/m^3 groundwater: max. 41 mg/l

Spread of pollution
  - liquid phase
  - plume
	
	not known
	not known

Remediation	withdrawal and cleaning (stripping) of groundwater since 1988; suction and clean up (activated carbon) of soil gas since 1988 with interruptions

Shallow soil sampling in the barrel storage area of the needle factory in 1987 showed tetrachloroethene contaminations of up to 2.6 g/kg.

In 1989 two soil gas samples were taken from new holes in a rubber factory nearby (B in fig. 13). Only background values were found. In spite of these results further investigations were planned because of suspicions that sampling procedures applied may not have been adequate.

– Remediation

Starting in March 1988 with three suction wells and with only two suction wells since 1994 vapour extraction methods are been applied for clean-up of the unsaturated zone at changig positions under the three source areas. About 920 kg DNAPLs had been removed until March 2001. Because of the fine-grained formation the soil gas suction could only operate intermittently with greater time intervals. The consultant hopes that due to contaminant extraction

from a new well installed in March 1993 and thus now thicker unsaturated zone the clean up efficiency will become greater in the future. Favourable is also, that since March 1995 the needle factory does not yet degrease with DNAPLs.

Remediation of groundwater started in May 1988 with intermittent pumping in hole 1 and mostly in hole 2, much of the time the holes are dry. Until April 1993 only 5,5 kg DNAPLs have been removed because of unfavourable well hydraulics. Therefore, a large-diameter well was constructed in March 1993. Since the begin of its operation in May 1993 about 49 kg DNAPLs habe been removed until March 2001, the level of DNAPL concentration in the abstracted groundwater is more or less constantly about 3000 µg/l. Because since then the contaminant sources are hydraulically contained, the DNAPL concentration in the plume is slowly decreasing.

Total costs were US$ 200,000 so far for the removal of about 975 kg DNAPLs in 13 years.

– Comments

The interpretation of the data suffers from a lack of detailed investigations. For instance, no observation holes were installed in the upper 4 m of weathered rock close to the site of pollution. There was no decicated attempt made to find the liquid phase. There is a lack of geologic investigations in regard to jointing and faulting patterns. The hydraulics of the groundwater flow system(s) are not clearly known.

It was assumed by the consultant that liquid phase and dissolved contaminants did not travel significantly into the red formation, but for this assumption there is no real reason. The few boreholes were installed in all likelihood missed highly permeable vertical fractures. In these fractures, liquid phase and dissolved plumes could spread unnoticed. The same could happen in the zone of weathering. Holes 10 and 11, low in contamination, may have missed transport pathways because the screens may be positioned too deep and below these pathways. The remediation well installed in 1995 and substituting the former small-diameter monitoring hole 2 has a depth of 28,5 m and therefore is sceened in compact hardrocks, too.

The unsatisfactory remediation activities are not only due to the unfavourable geological features, but also to the lack of money. The factory nearby in NE direction (C in fig. 13), also responsible for another groundwater deterioration and obviously contributing to the solvent amount exstracted at area A, went bankrupt. Over a longer period, the company A had financial problems, too, so that only sinze 2001 an optimization of remediation efforts is possible.

• City of Hadamar

– History and geology

When drinking water standards were changed, an investigation of the City of Hadamar water supply (hole 4 in fig. 14) in 1983 showed a small content (> 25 µg/l) of tetrachloroethene. In a nearby spring (observation point 5 in fig. 14) the content of DNAPLs was found to be higher (up to 40 µg/l). Further investigations revealed that a textile company 200 m away was the source. The company operated from 1966 to 1986.

The sources of pollution were cleaning and distillation facilities, leakage from solvent pipelines, a barrel storage area, and an area where textiles were softened with tetrachloroethene for welding. At the main point of pollution the liquid phase had moved into a cable duct and from there directly into the soil. Detailed estimates of the total amount of leakage were attempted by the Solicitor General without success. From general deductions the losses can be estimated to be between 50 and 150 tons of liquid.

The factory is located in hilly terrain on 5 to 8 m of loess above 2 to 3 m of gravel, with clay underneath (fig. 14, holes 1, 2). Clay was not penetrated by drilling to prevent leakage of liquid phase into the deeper subsurface. Karstic limestone is, however, known to exist underneath. The lithologic profile in the nearby hole 3 consists of 7.5 m of silt and 6 m of diabase tuff over limestone.

1 alluvium, 2 loess/loes loam, 3 hillslope mass, 4 fluviatile sediments (sand, gravel) of t_1-terrace, 5 fluviatile sediments (sand, gravel) of t_3-terrace, 6 clay, 7 silt, 8 diabase tuff (Devonian), 9 limestone, karstic (Devonian), 10 fault, 11 groundwater table
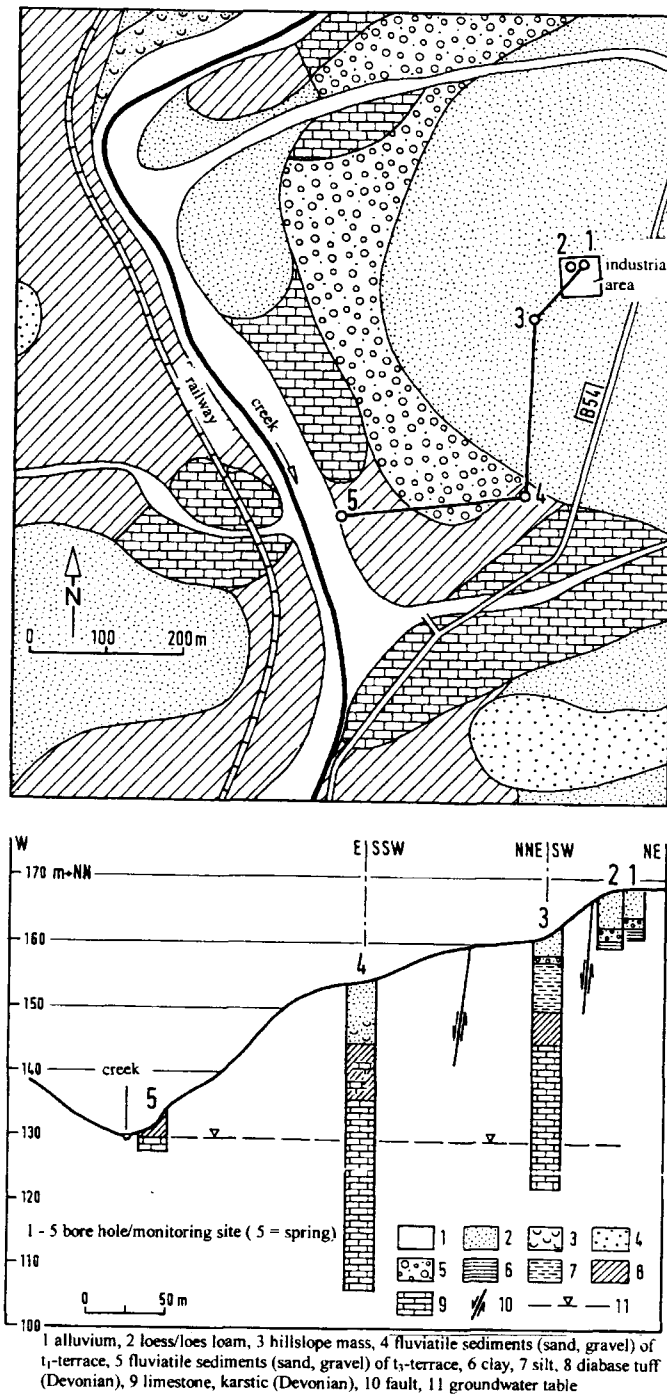
Figure 14: Contamination by DNAPLs in karstic rocks, City of Hadamar. Upper part: geologic map, lower part: cross-section.

Spring 5 only flows when water supply pumping in well 4 is reduced. The water table in the limestone is at about 30 m depth in monitoring well 3. Perched groundwater occurs in the overlying unconsolidated rocks. Flow connections exist between the perched groundwater

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body and the groundwater in the limestone. Their exact locations and mechanisms are not known.

– Investigations

Following the original investigation of groundwater in monitoring well 4, monitoring well 3 was drilled into limestone in December 1984. Monthly samplings showed pollution values between 200 and 600 µg/l. Spring 5 showed values from 20 to 40 µg/l.

From 1984 to 1986 about 30 test holes were drilled from 5 to 8 m depth for one-time soil gas sampling to locate the source of pollution within the compounds of the textile company. Analyses showed up to 2.9 g/m^3 of tetrachloroethene content.

Eight core borings were undertaken in 1985 and 1986 through the concrete of the factory floors into the soil underneath. Pollution was up to 3 g/kg. No attempt was made to investigate for macropores or jointing.

Table 8: Synoptic summary of subsurface pollution by DNAPLs at the City of Hadamar

CASE	City of Hadamar
Case	City of Hadamar karstic rocks textile plant
Sources of contamination	cleaning and distillation facilities, leakes in pipes, barrel storage area for solvents
Type of DNAPLs	tetrachloroethene
Start of leakage	possibly since 1966
Geology/Hydrogeology	karstic limestone and diabase tuff (Devonian), overlain by clay (Tertiary), gravel and loess (Quarternary)
Depth to water table	upper aquifer in gravel: 7 - 8 m main aquifer in limestone: appr. 30 m
Coefficient of permeability	not known
Field velocity of groundwater	not known
Type of investigation	soil: 8 cored boreholes in loess soil gas: 30 samples in loess groundwater: 1 monitoring well in limestone installed
Degree of pollution	soil: max. 2.9 g/kg soil gas: max. 2.9 g/m^3 groundwater: max. 0.6 mg/l
Spread of pollution - liquid phase - plume	 not known length at least 0.5 km (exact extend not known)
Remediation	cleaning of drinking water since 1986 suction and clean up of soil gas in 1986 and 1985

– Remediation

The first goal of remediation was the removal of dissolved plume from the perched groundwater body within the diabase tuff. To achieve this goal, hole 3 was drilled before any drilling at the factory site took place. Since the permeability of the tuff proved to be low, the hole was deepened into the limestone for monitoring purposes. No sample was taken from the gravel

layer encountered in the higher part of hole 3, nor any additional hole installed in this gravel for monitoring or remediation purposes.

No attempt was made to clean the groundwater near the factory, neither in the perched groundwater body nor in the limestone. Instead, since May 1986 until today the water from the water supply well 4 was air stripped (pollution at the begin of the remediation activities > 25 µg/l, now contents changing between 10 and 20 µg/l). The amount of DNAPLs extracted there is recorded, but a balance was not kept, because hydrogeology and hydraulics of a karst water body are very difficult.

Vacuum extraction by six soil air suction wells was undertaken from August 1986 to July 1987. By August 1987 the soil gas values were low. The regulatory agency therefore allowed the vacuum extraction to be permanently discontinued. About 70 kg of tetrachloroethene has been extracted.

Originally, excavation of the polluted soil was ordered by the regulatory agency. Excavation of the estimated volume of 4,800 m^3 of polluted material would have cost about US$ 2.7 million. Bankruptcy lawyers, however, successfully argued in court that excavation should be replaced by the much less expensive soil gas extraction. But this was not done.

Total costs for investigation were US$ 60,000. Because it could not be clearly shown that the groundwater pollution was caused by the company, 50 % of the costs were carried by the state of Hesse. For the same reason, the City of Hadamar carried the total costs for clean up of the water supply. By 2000, the costs exceeded US$ 120,000.

– Comments

In the eyes of the regulatory agency this case has been properly investigated and cleaned up. It is clear, however, that the flow path and fate of the liquid phase are unknown. The observed reduction of pollution in continous suction of soil air is normal and does not mean the soil has been cleaned. Instead, intermittent pumping would be required to extract additional volatiles migrating from the fine into the coarser pores.

The extent and even location of the plume of contamination within the groundwater body is still not known. None of the recommended geophysical methods for locating water-filled karstic systems have been applied, nor any tracer test to find other exits from the karstic water system than the known spring 5 and the pumped borehole 4.

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