Guideline for Groundwater Risk Assessment at Contaminated Sites (GRACOS)

Recommendations for the assessment of a potential risk of groundwater pollution originating from a soil contamination in the unsaturated zone

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Introduction

This guideline contains recommendations how to assess a potential risk of groundwater contamination originating from a pollution in the unsaturated soil zone. Two base cases are distinguished as typical source scenarios (Fig. 1) :

1. Residual non-aqueous phase liquid (NAPL) held by capillary force allowing diffusive spreading of volatile constituents in the unsaturated zone and eventually groundwater contamination. This scenario was investigated in high detail in a controlled field experiment conducted in Denmark employing a kerosene type organic liquid mixture of volatile hydrocarbons (Part I).
2. Layers of contaminated top soils or disposed waste materials, which release contaminants into the seepage water. For this scenario leaching tests were developed/optimised and validated for organic and inorganic pollutants. The release dynamics were investigated in long term leaching tests and simulated using numerical models (Part II).

The recommendations derived are based on the experience of the researchers involved, including additional knowledge gained during the GRACOS project. For the sake of brevity and readability, the guidelines do not contain comprehensive data sets, detailed description of theories, literature, etc. These supplementary materials are supplied in reports and numerous publications of the project (see http://www.uni-tuebingen.de/gracos).

In addition, the appendix provides a list of symbols and abbreviations, the complete references published by the GRACOS consortium, data from experiments and databases used, short descriptions of the numerical codes used, and procedures for leaching of soil and waste materials for the assessment of mobility/bio-availability of toxic compounds. In addition, Table A.2 (pp. 54) provides a comprehensive compilation of physical-chemical properities of the compounds addressed in GRACOS. The GRACOS web-page (http://www.uni-tuebingen.de/gracos) provides further material for download and a variety of video clips on the dynamics of vapour spreading and leaching.

These guidelines were discussed and approved by members of the GRACOS external advisory committee. The help of K. Dahlström (Denmark), A. Ginebreda (Spain), R. Hahn (Germany) and U. Ziegler (Switzerland) is greatly appreciated.

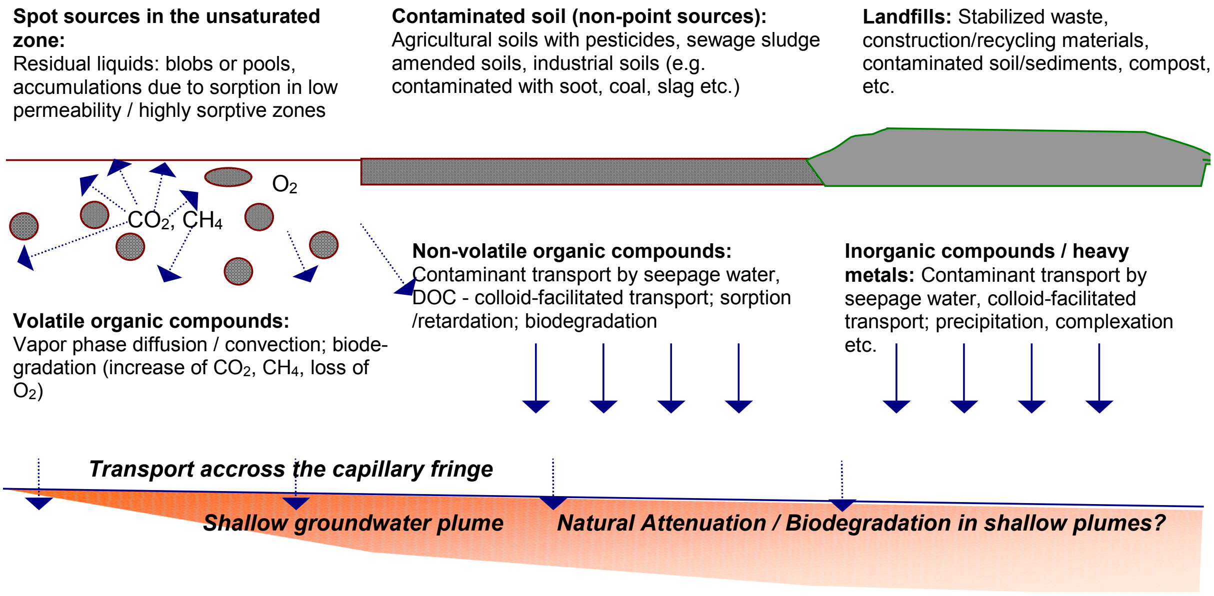


Figure 1: *Most relevant pollution scenarios and transport processes of the different compound classes to the groundwater table. Left: Residual organic liquids (e.g. fuel) trapped in the pore space. Volatilised hydrocarbons spread by diffusion laterally and vertically. This causes contamination of the unsaturated soil and possibly the groundwater. Centre and Right: Contaminated soils and other materials (e.g. waste) cause pollution of seepage water depending on sorption capacity of the soil/waste material and the properties of the compound. Relevant for groundwater risk assessment is the contamination to be expected in the aqueous phase and not the contamination concentration in the solids.*

Part I Volatile Pollutants in the Vadose Zone

Lead Authors: Peter Kjeldsen, Mette Broholm, Mette Christophersen

I.1 Characterisation of VOC contaminated sites

Organic liquids are frequently spilled in the unsaturated zone, e.g. at gasoline stations or other fuel storage sites etc... Its constituents often have high vapour pressures, leading to volatilisation to the soil air and spreading by diffusion and in very coarse grained material by pressure driven gas advection. In order to evaluate the risk for groundwater contamination from such pollutants, investigation of the pollutant distribution in the gas, water and solid phase needs to be carried out. The spatial distribution of the pollutants either as sorbed pollutants on the solids or non-aqueous phase liquids (NAPLs) may be of a very heterogeneous nature. Of the two mobile phases in the vadose zone, gas and water, the gas phase has the largest potential for spreading due to much higher diffusion rates and advection velocities. Besides, sampling of pore air is in most cases much easier in comparison to pore water. This chapter will mainly focus on a method and techniques for pore gas sampling, but will briefly discuss methods and techniques for pore water sampling. Sampling of polluted soil will not be included. The chapter gives, besides a description of the more technical sides also ideas to strategies for delineating pollution distribution in the vadose zone. It focuses only on the groundwater contamination risk related to the soil contamination. Other risks such as indoor health are not covered.

I.1.1 Plume mapping in the vadose zone

Spills of volatile organics into the subsurface may lead to severe groundwater contamination. For large spills of NAPLs a separate phase may be transported into the groundwater zone by gravitational forces. A significant residual separate NAPL phase, however, always is left in the vadose zone. For smaller spills the whole spill may remain in the vadose zone. Residual separate phases of LNAPLs or DNAPLs are sources for spreading of volatile pollutants by volatilisation from the source and gas transport away from the source, or - for water soluble pollutants - by direct dissolution into rainwater which infiltrates the source zone. Fig. I.1.1 shows the conceptual model for the spreading and attenuation processes of a NAPL source in the vadose zone. As indicated in the figure, the plume of volatile pollutants is potentially a source to enhanced groundwater contamination because of leaching of the soluble contaminants by infiltrating water in a much larger area than the area of the NAPL source itself. The objective of mapping the plume in the vadose zone is to assess the size of a potential source of groundwater contamination. This evaluation may be carried out by installation of a network of pore water samplers sampling directly the soil pore water (see section I.1.2.2). This is, however, an expensive, challenging and laborious solution. Instead, the volatile pollutant concentration in the pore air can be mapped by installing pore gas probes (see I.1.2.1) and then calculating the soil water concentration assuming validity of the *Henry´s* law. On the basis of the mapped plume of volatile compound in the soil gas, indications of the presence of free NAPL phase in the vadose zone may be obtained. An analysis of the free phase magnitude and composition may be a next step taking soil samples.

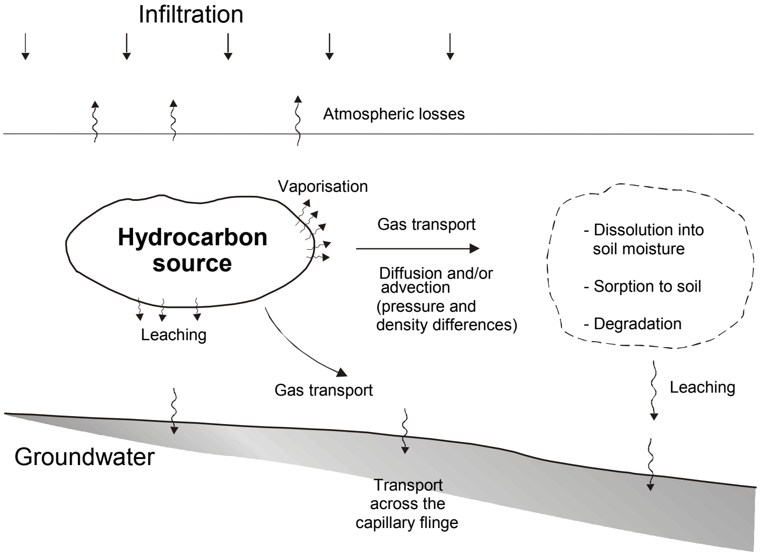


Figure I.1.1: *Conceptual model of the processes governing the pollutant transport and attenuation at a hydrocarbon source in the vadose zone.*

The mapping can be carried out by special equipment, profiling the concentration distribution in the vadose zone without leaving fixed gas probes. Compared to the technique of sorption to carbon tubes and extraction with an extraction agent, this technique can be combined with a direct or indirect analysis of the pore air content either by a transportable GC or MIP (membrane interface probe) system, which either on site or *in situ* obtains a signal for the pollutant content in the pore air. The advantage of this approach is that it is quick and relatively cheap. However the disadvantage is that no fixed installations are left in the ground that may be used for future plume delineation or evaluation of potential remedial actions carried out towards the source.

I.1.2 Monitoring and sampling techniques, instrumentation and analysis

Probes for pore gas sampling

Installations for pore gas sampling can be divided in:

- Pore gas probes
- Pore gas wells
- Passive accumulating devices

Pore gas probes are tubes (either metal or hard plastic) that are hammered or pressed into ground down to the desired depth by hydraulic, pneumatic or manual techniques. Pore gas probes were the technique used at the GRACOS field site. The tube can be slotted at the bottom and equipped with a conical tip to facilitate the installation. The probe can also be equipped with a loose tip. For this kind of probes the tube is withdrawn a little bit after installation to desired depth to open the bottom hole of the tube. This type is only for instant gas sampling.

Pore gas wells are equivalent to traditional groundwater wells made by a drill rig including installation of a larger diameter well (typical 1-3”) with screen, sand pack and bentonite plugs.

Passive accumulating devices are devices containing either a semi-permeable or permeable membrane. The devices with semi-permeable membrane allow only diffusional transport of pollutants into the membrane and leads to an accumulation of pollutant in the collecting chamber behind the membrane. These are useful for monitoring the presence of pollutants having low volatility. For the device with a permeable membrane equilibrium is established between the soil gas and the air chamber behind the membrane. Both devices need to be installed in situ in close contact to the soil.

Probes for pore water sampling

Pore water may be sampled from the unsaturated zone by installation of porous cups, which by capillary forces suck water out of the unsaturated soil. A proper contact between the porous cup and the unsaturated soil can be obtained by addition of fine silica flour around the porous cup. The volume of silica flour should be kept to a minimum since the water in the silica flour must be purged prior to sampling. The porous material should be made in inert material such as sintered stainless steel or ceramics. Such probes were installed at the GRACOS field site. Experiments conducted during the GRACOS project with porous cups made of Teflon have shown that these cups have a considerable sorbing capacity and cannot be recommended for hydrophobic organic compounds.

Other instrumentation of the vadose zone

The water content of the unsaturated soil is an important factor for the diffusivity of the soil and therefore for the ability of the soil layers to spread volatile pollutants by diffusion. Water content can be measured by “destructive sampling” taking soil samples and measure the water content gravimetrically in the laboratory. Also non-destructive methods exist. The most common are neutron-logging and Time Domain Reflectrometry (TDR). For water content determination by TDR, pairs of metal rods are installed in different depths in the unsaturated soil. By use of a cable tester and a appropriate software, the volumetric water content can quickly be determined. At the GRACOS field site both soil sampling and TDR technique were used. The results show that at relative dry conditions (below a volumetric water content of 8%) TDR has a tendency to overestimate the water content. At higher water content a good correlation between TDR and direct soil sampling was obtained.

Gas sampling for major gases and VOCs

Methodologies. The gas from the unsaturated soil volume surrounding the screened section of the soil gas probe is sucked into the sampling tube by supplying a vacuum using a gas pump. Before sampling the probe should be purged in order to remove standing gas in the soil gas probe. In some cases the gas may be analysed directly by attaching the gas stream to the instrument. In this case no sampling is needed.

Containers. The gas can be sampled in basically three ways:

- Gas collected in flexible *gas bag*
- Gas collected in evacuated sampling container
- Pollutants collected on *adsorptions cartridges*

The three different ways are shown in Fig. I.1.2. Gas bags are often made by relative inert material such as Tedlar for minimising losses due to diffusion out of or sorption to the polymer material. Evacuated sampling containers are often made of inert material such as stainless steel or glass. Initially, they are evacuated to near complete vacuum and may be filled slowly with gas from the soil gas probe through an adjustable valve. As an alternative to sampling the whole gas sample in a container, the pollutants of interest may be trapped in tubes containing a sorbing material– or several materials in combination - with capability of retaining the pollutants. The pros and cons of the different containers are summarised in Table I.1.1. At the GRACOS field site stainless steel tubes with a mixture of two sorbents were used for VOC characterisation, and evacuated blood test tubes for the major gases. These techniques can generally be recommended also for plume delineation on a more routinely basis.

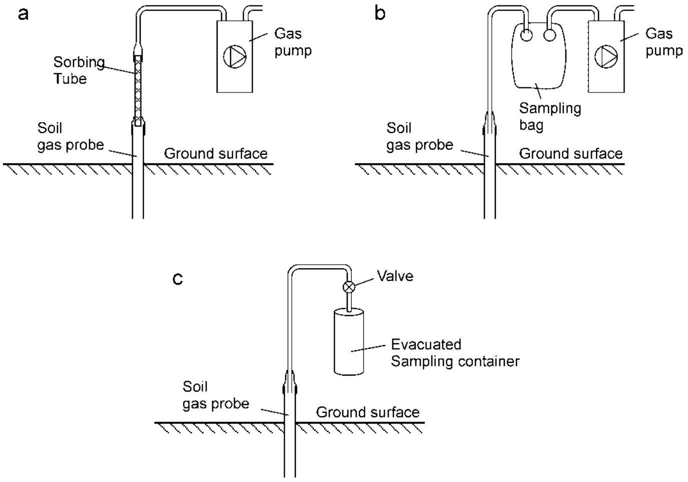


Figure I.1.2: *Three alternative systems for taking soil gas samples from the vadose zone using a) an adsorption cartridge, b) a flexible sampling bag, and c) an evacuated sampling container.*

Table I.1.1: *Pros and cons of gas sampling containers.*

Methodology	**Pros**	**Cons**
Flexible bag	Relatively cheap No pre-evacuation needed	Relatively short storage time
Evacuated container, blood test tubes	Cheap Small volume Easy to transport and store	Relatively short storage time Best for major components (O_2, CO_2, N_2, CH_4) Loss by sorption to rubber stoppers Sample contamination from compounds in rubber stoppers Pre-evacuation needed Non-used containers have limited durability
Evacuated container, stainless steel	Relatively long storage time	Relatively expensive Often large volumes which are bulky to transport
Adsorption cartridges	Easy to transport/store Long storage time Can be used for less volatile Hydro- phobic compounds such as alkanes Low detection limit by passing large gas volumes through the tube	Selective, may not retain all compounds or the whole mass of pollutants in the gas volume especially at high gas concentrations (breakthrough)

Pore water sampling for VOCs

Methodologies. A constant low pressure can be supplied to the porous cup by attachment to a vacuum container at the surface. In this way the water is collected in the container at the soil surface. Care should be taken for very volatile compounds since a considerably loss may take place to the headspace in the container. In this case an extraction agent may be added through a septum without opening the container prior to extraction. For relative coarse materials and while sampling low pressure may only be supplied by use of a vacuum or peristaltic pump. Overflow for some time may be advantageous to avoid losses to headspace. Fig. I.1.3 shows the two methodologies. Care should be taken to avoid materials that may absorb the organic pollutants. Teflon based porous cups have been shown to significantly sorb the pollutants leading to biased results. Materials like stainless steel and ceramics are the only materials that have been proven not to retain organic compounds. Pore water sampling for VOCs are a much more difficult and time-consuming method in comparison to pore air sampling. For characterisation of VOC on a routinely basis the use of pore air sampling techniques and calculation of pore water concentration using *Henry´s* law is recommended. Here it is important to use well-documented *Henry´s* law constants at the soil temperature at sampling time.

Gas analysis for major gases and VOCs

If only a relative low precision of the gas analysis for the major components (oxygen, carbon dioxide, nitrogen and eventually methane) is required, the gas may be analysed in the field by an IR-detector directly attached to the soil gas probe. Higher precision can be obtained by use of a portable GC for the major gases. Gas can be taken directly from the gas stream by a syringe through a septum for direct injection on the GC.

For gas sampled in bags or canisters the analysis of the gas for VOCs is often performed by direct injection of a sub sample taken from the container by an injection syringe to a GC. The GC may be combined with different detectors (FID, ECD or MS) depending of the compounds in focus. Gas sampled in sorbing tubes needs to be desorbed before analysis on a GC. This is done by an ATD (Automated Thermal Desorber) unit which is attached to the injection port of the GC. For large sampling programs the use of field GCs or mobile laboratories may be of advantage due to less transport and faster results, which may be used interactively for gas plume delineation.

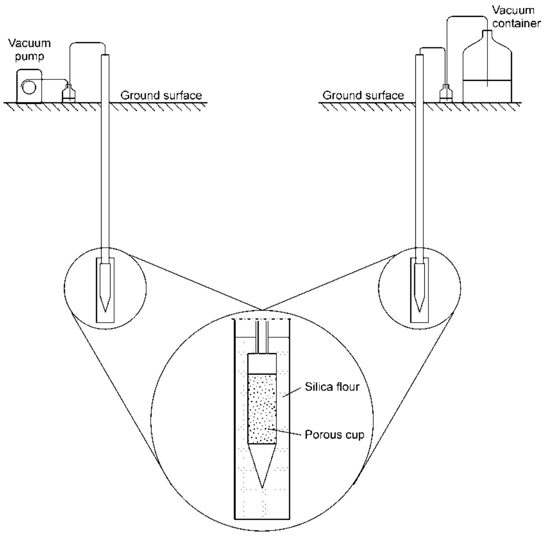


Figure I.1.3: *Two alternative systems for taking pore water samples from the vadose zone using a porous cup.*

Lessons learnt and recommendations

Characterisation of VOC contaminated sites:

- ✓ The objective of mapping a plume in the vadose zone is to get delineation of the potential source area for a groundwater contamination.
- ✓ Instead of using expensive and laborious pore water samplers, the **volatile pollutant concentration in the pore air** can be mapped by installed **pore gas probes**. The soil water concentration can be calculated based on ***Henry´s law***.
- ✓ That fact that *Henry´s law* is valid, is corroborated by the good agreement of field measurements and numerical modelling as the latter relies on the local equilibrium assumption between soil, air and pore water (i.e. mass balances are calculated by *Henry´s law).*
- ✓ The **mapping** of soil pore air can be carried out with a special equipment, profiling the concentration distribution in the vadose zone without leaving fixed gas probes. This **quick and relatively cheap technique** can be combined with a **direct or indirect analysis of the pore air concentration** either by a transportable GC or MIP (membrane interface probe) system.
- ✓ For **pore gas sampling, stainless steel probes** can be used. These probes are **cheap and easy to install**. Other sampling devices are pore gas wells and passive accumulating devices, which require more expense for installation.
- ✓ The **water content of the unsaturated soil** is an important factor for the diffusivity of the soil and therefore for the ability of the soil layers to spread volatile pollutants by diffusion. A non-destructive method is time domain reflectometry (TDR). A **calibration of the TDR soil moisture measurements by gravimetric measurements** is recommended.

I.2 Biodegradation of VOC in the vadose zone

Lead Author: Patrick Höhener

I.2.1 Conceptual model

The unsaturated zone is a porous filter layer in which microbiological processes play an important role for the natural attenuation of pollutants. To better understand the microbial processes, it is first important to gain an insight into the spatial distribution of microorganisms and pollutants in the unsaturated zone. Accidental releases of NAPLs in small quantities to the subsurface result usually in residual fuel pools retained in the unsaturated zone. Volatile compounds evaporate from fuel and migrate as vapour through the unsaturated zone by diffusion and/or advection. The vapour phase is thought to be in equilibrium with the aqueous phase via Henry’s law. Microorganisms can uniquely live in the aqueous phase, and thus also the biodegradation process is located in the aqueous phase as illustrated in Fig. I.2.1.

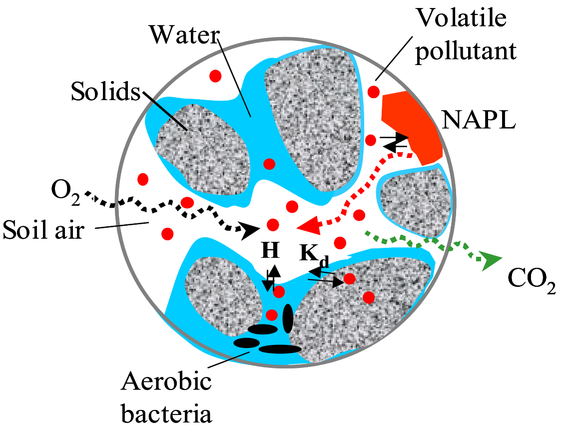


Figure I.2.1: *Conceptual model for VOC biodegradation in unsaturated porous media. H: Air-water equilibrium partitioning (Henry coefficient); Kd: Water-solid equilibrium partitioning; broken arrows: vapour-phase diffusion.*

The soil gas in the unsaturated zones contains O_2, and therefore the most important biodegradation processes are aerobic processes. The aerobic biodegradation of common pollutants has generally been studied well in the laboratory using pure or mixed bacterial cultures. Many organic compounds can be completely transformed to harmless inorganic constituents (CO_2, H_2O, Cl^-). This process is called mineralisation and is the most important process underlying the natural attenuation of pollutants. The general stoichiometry of the aerobic mineralisation of an organic compound composed of carbon, hydrogen and oxygen is given in the following equation (under the assumption that no microbial biomass is formed):

$$C_xH_yO_z + (x+y/4-z/2)\ O_2 \rightarrow x\ CO_2 + y/2\ H_2O.$$

Example: To mineralise 1 kg of benzene, a mass of 3.1 kg of O_2 is required, corresponding to the O_2 in 19 m^3 of ambient air at 25°C. From this mass relation it is easily understood that in **highly contaminated unsaturated zones** with restricted aeration, the **biodegradation processes may get limited by the lack of oxygen.**

When the diffusive or advective supply of O_2 from the atmosphere to the soil is lower than consumption rates by aerobic processes in the soil, then anaerobic conditions may establish. In the absence of O_2 microorganisms use alternative electron acceptors, and the following processes are occurring: Denitrification (reduction of NO_3 and NO_2^- to N_2O and N_2), manganese and iron reduction to Mn^{2+} and Fe^{2+}, sulfate reduction to sulfide, and methanogenesis (reduction of CO_2 to CH_4). However, anaerobic mineralisation processes are generally slower than aerobic processes. Therefore, engineered bioremediation technologies of unsaturated zones contaminated by biodegradable organic pollutants rely often on aeration, e.g. by air injection.

I.2.2 Occurrence of microorganisms in the unsaturated zone

Direct microscopic counts of bacteria in pristine unsaturated zones vary from 10^4 – 10^7 bacteria per gram, with typically lowest values in low recharge areas. In saturated porous aquifers, the corresponding numbers are generally higher, ranging from 10^5 – 10^8 bacteria per gram aquifer sediment. Depth profiles were e.g. studied at a pristine site in Oklahoma with 3 m of unsaturated zone in summer and winter. It was found that biomass and activity of bacteria and protozoa was seasonally constant, declined sharply with depth, reached a minimum in the unsaturated zone and rose occasionally in defined layers in the saturated zone. In another pristine unsaturated zone of 26 m thickness in the US Midwest, the lowest biomass and small biodegradation rates of glucose and phenol were found in unsaturated tills, compared to higher values both in topsoil and in the saturated zone. In contaminated unsaturated zones, microscopic counts of bacteria are typically higher than at uncontaminated sites. However, it should be noted that the detection and quantification of microbial cells in the unsaturated zone does not yet allow quantifying and predicting biodegradation rates, since a considerable percentage of cells were found to be in inactive physiological states and because degradation may be limited by transfer rates of oxygen or the bio-availability of the pollutant.

I.2.3 Microbial activity

Consistent with lower availability of carbon substrates and nutrients, the microbial activity is lower in the unsaturated zone compared to top-soils. Slower turnover rates and longer lag times were observed when labelled natural carbon sources were introduced to subsurface microbial communities in laboratory microcosms. However, the detection of microbial activity in laboratory incubations was found to be highly dependent on factors such as incubation time, nature of the substrate, type of assay, and sample storage prior to initiation of the assay. In situ methods to quantify microbial activity in the unsaturated zone are thus preferable. Using geochemical mass balance models, in situ microbial turnover rates of natural carbon substrates can be quantified using CO_2 production rates.

I.2.4 Methods to assess and quantify biodegradation

The experimental basis to understand biodegradation rates and kinetics of VOC vapours in the unsaturated zone is still limited. Many studies were based on laboratory batch microcosm experiments. Limitations of batch techniques include breakdown of soil aggregates, changing boundary conditions (e.g. O_2) and the use of soil-to-contaminant ratios that are much smaller that in natural soil systems. Laboratory soil column experiments can avoid some of these limitations and can account for transport and degradation. Unsaturated laboratory column experiments have been performed with vapour transport being solely diffusive or advective and diffusive. Due to a lack of reliable methods to measure rates at field sites no systematic study that compares laboratory-determined rates with in situ rates has been performed so far. In addition to laboratory methods, mathematical models have been fitted to concentration profiles observed at contaminated field sites to estimate in situ biodegradation rates. However, this approach is difficult to apply in heterogeneous field situations, it requires complete concentration profiles, and is not applicable to estimate the biodegradation potential at uncontaminated sites. Furthermore, the biodegradation rate is calculated based on mass flux considerations and therefore, uncertainty in calculating mass fluxes (e.g. due to uncertainties in effective diffusion coefficients) are incorporated into the estimated biodegradation rates.

I.2.5 Biodegradation rates and their dependency on environmental parameters

In the appendix, measured biodegradation rates for volatile organic compounds in different unsaturated porous media using various experimental techniques are reported. It is very difficult to generalise biodegradation rate data for unsaturated zones. The wide range of data illustrates that the rates depend on various environmental or compound-inherent factors affecting the biodegradation rates, which are discussed below.

- *Biodegradability of the contaminants*: Depending on the enzymatic systems of the microorganisms to catalyze the biodegradation processes, degradation rates of volatile organic compounds are largely differing. For aerobic degradation, the following general order of decreasing reactivity has been observed: monoaromatic and unbranched aliphatic hydrocarbons > cyclic aliphatic hydrocarbons > polyaromatic hydrocarbons and branched aliphatic hydrocarbons.

- *Bio-availability of the contaminants*: Contaminants that have low aqueous solubilities or are sorbed to solid surfaces, or remain in free phase as crystals or NAPL droplets are usually not accessible to microorganisms.

- *Concentration of the contaminants*: Conflicting findings were obtained with unsaturated experimental systems, as first-order as well as zero-order biodegradation kinetics were reported for various compounds. When the aqueous concentrations of organic pollutants are low, then first order kinetics are expected. First order kinetics often are the most robust and simplest choice for modelling VOC biodegradation.

- *Temperature*: For temperature relationships, several expressions have been described, of which Q_{10} and Arrhenius relationships are the most frequently used. Note that most laboratory rate data are available for 20-25°C, whereas temperatures in unsaturated zones of > 1 m depth in temperate regions are rather in the region of 10-15°C.

- *Oxygen*: The effect of O_2 concentration on biodegradation rates can be expressed using a Mono-type equation, with typical half-saturation constants for O_2 of 0.1-0.2 mg/L in aqueous solutions. Assuming that the soil water is in equilibrium with soil air, then typical half-saturation partial pressures of O_2 in soil air are 0.001-0.002 atm.

- *Water content of unsaturated zone*: In soil jar and lysimeter experiments with hydrocarbon-contaminated soils, the water content could not be identified as a direct governing environmental factor for water contents above 10% (v/v). Only in very dry soils, water becomes a limiting factor. An indirect effect of water content is, however, that it influences the effective gaseous diffusion coefficient in unsaturated porous media, influencing thus also the O_2 availability.

- *Nutrients*: Nitrogen, phosphorus, sulfur, potassium, calcium, magnesium, or iron is needed to support the growth of microorganisms. Most nutrients are usually present in sufficient amounts in topsoils, but may be lacking in lower strata. Batch experiments clearly showed a stimulating effect on toluene or gasoline biodegradation rates in soil when adding NH_3 and PO_4^{3-}.

- Toxicity: High aqueous concentrations of contaminants can pose toxicity problems for biodegradation, especially at spill sites with pure products. When the NAPL is a mixture such as petroleum products, then the effects of Raoult's law lower the gaseous and aqueous concentrations of individual compounds below limits where toxicity effects are observed.

Lessons learnt and recommendations

Biodegradation of VOC in the vadose zone:

- ✓ **Microorganisms** can exclusively live in the **aqueous phase**. Therefore, also the **biodegradation process is located in the aqueous phase.**
- ✓ Since the soil gas in the unsaturated zones contains O_2, the **most important biodegradation processes are aerobic processes.**
- ✓ In addition to laboratory methods, **mathematical models have been fitted to concentration profiles observed at contaminated field sites to estimate in situ biodegradation rates**. However, this approach is **difficult to** apply in heterogeneous field situations. It requires complete concentration profiles, and is not applicable to estimate the biodegradation potential at uncontaminated sites.
- ✓ It is **very difficult to generalise biodegradation rate data for unsaturated zones**. A wide range of data illustrates that the rates **depend on the following various environmental or compound-inherent factors** affecting the biodegradation rates: Biodegradability and bioavailability of the contaminants, concentration of the contaminants, temperature, oxygen, water content of unsaturated zone, nutrients, toxicity.

I.3 Scenario specific modelling of spreading of VOC plumes

Lead Authors: Petros Gaganis, Vasilis Burganos

I.3.1 Introduction

Modelling flow and transport of VOCs in the unsaturated zone is scientifically and technically challenging. The unsaturated zone contains multiple fluid phases through which VOCs may move, as well as associated interfaces for partitioning between phases. For example, when water, air, NAPL, and an immobile solid phase are present, three mobile phases may occur with as many as six interfaces (four, if water is completely wetting) for contaminant interface mass transfer. Additional difficulties arise when sites contain complex mixtures of organic compounds that may involve interactions among phases, interfaces and chemical components. These interactions will likely influence multiphase flow and transport processes, interface mass transfer rates, contaminant loading rates in the saturated zone, as well as bio-availability of contaminants. However, using relatively simple public domain simulators, many problems in transport modelling of the vadose zone can be reasonably well addressed by understanding the dominant aspects of the problem. Here, the relative effect on the transport and fate of VOC mixtures in the vadose zone of the most important factors is investigated and quantified using scenario specific numerical modelling with the emphasis placed on the development of simple rules and guidelines for a rapid assessment of the potential risk of contamination. The simulated scenarios include the EPFL lysimeter experiment and the DTU field tracer test, as well as theoretical scenarios like the one shown in Fig. I.3.1.

I.3.2 Various factors that influence the spreading of VOC plumes

The factors and processes that may influence the spreading and the fate of VOC mixtures in the unsaturated zone are (i) the soil type (different soil moisture profiles and hydraulic properties), (ii) recharge rates, (iii) sorption and biodegradation, (iv) source location relative to ground surface and the water table, (v) different VOC mixture composition, and (vi) mass transfer among phases following a first order rate of 0.1 d^{-1} instead of equilibrium partitioning. The results of various simulations are presented in terms of soil gas concentrations and in terms of time to depletion of each mixture compound from the residual source. Fig. I.3.1 shows the sampling locations and the base case hydrogeological setting adopted in these simulations while the NAPL source consists of the VOC mixture shown in Table I.3.1.

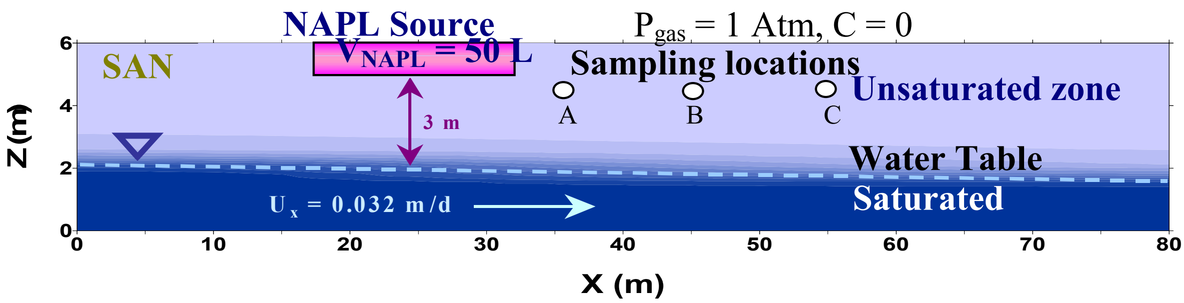


Figure I.3.1: *Schematic illustration of the base case theoretical scenario used for the numerical investigation of various factors affecting VOC spreading in the vadose zone.*

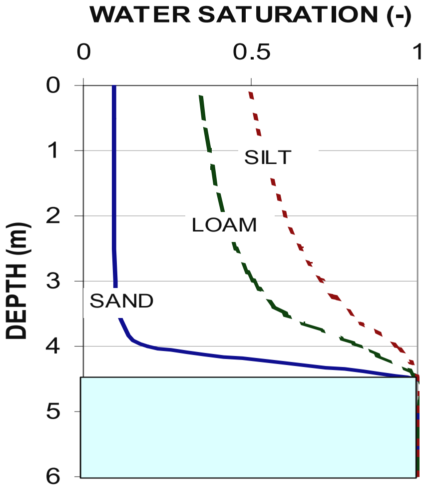


Figure I.3.2: *Soil moisture profiles of selected soil types.*

Table I.3.1: VOC mixture composition and physical-chemical properties (for more compound see Appendix 3).

Compound	Molecular weight (g/mol)	Weight fraction	Density (g/m^3)	Vapor Pressure [atm]	Solubility (g/m^3)	HENRY's partition coeff. (-)	Distribution coeff. $[m^3/g]$	Biodegradation rate (1/d)
Pentane	72.15	0.2	6.26E+05	0.5549	38.5	52.59	1.97E-07	0.016
Methylcyclopentane	84.16	0.2	7.42E+05	0.1389	42	14.85	1.10E-07	0.676
Benzene	78.11	0.2	8.76E+05	0.0993	1790	0.21	2.10E-08	0.200
1,2,4-Trimethylbenzene	120.19	0.2	8.80E+05	0.0021	57	0.19	2.53E-07	1.017
Decane	142.28	0.2	7.30E+05	0.0017	0.052	197.85	2.05E-04	97.025

The properties of the selected soil types and the corresponding soil moisture profiles are shown in Table I.3.2 and Fig. I.3.2, respectively.

Fig. I.3.3 shows the spreading of the gaseous plumes of the five simulated compounds 30 days after the release of 50 L of VOC mixture near the ground surface in sand when no recharge, sorption and biodegradation occur. The respective aqueous phase concentrations can be calculated as $Cw=Cg/H$, where H is the Henry's constant.

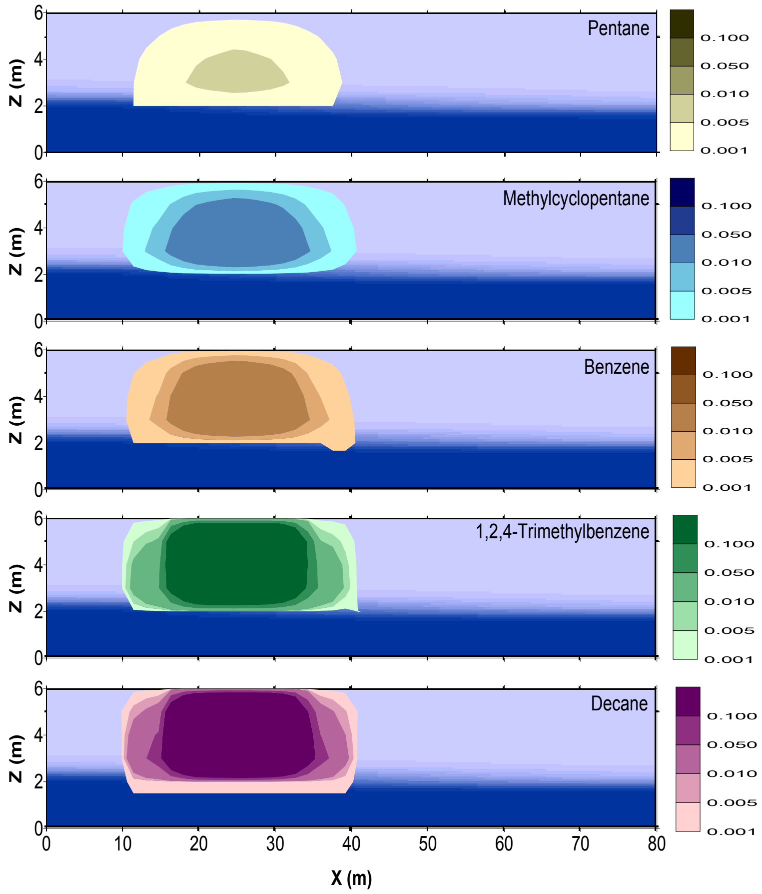


Figure I.3.3: *Normalised gaseous concentrations [*$C_{gn} = C_g$ x *(aqueous solubility* x *Henry's constant)] in sand of the five VOC mixture components at day 30 (see* http://www.uni-tuebingen.de/gracos *for animated simulations) .*

> ***Example:*** For a **NAPL spill of 50 L of a VOC mixture** in the subsurface, the **time to source depletion may range over several orders of magnitude**, from few days for the volatile compounds (e.g. pentane) to many years for those with low vapour pressure (e.g. decane).

In general, in the source gaseous phase plumes in sand, as defined by the 0.1% contour of the initial gaseous concentration in the source, rarely extend more than 8 meters distance from the source zone (Fig. I.3.3). In sandy soil, most mass diffuses to the atmosphere through direct volatilisation from the source, while the importance of this mechanism becomes smaller for loam and silt. The normalised maximum soil gas concentrations for each compound in the VOC mixture were calculated at different sampling locations. The sampling locations were situated in different distances to the source zone: Sampling location *A* 2.5 m, sampling location *B* 12.5m, and sampling location *C* 22.5 m from the source zone. Maximum calculated normalised concentrations at location *A* are in most cases at the level of 10^{-2} to 10^{-3}. Concentrations at location *B* are usually 1 order of magnitude smaller than that at location *A*, while concentrations at location *C* are 1 to 2 orders of magnitude smaller than that at location *B*. This indicates that gas phase diffusion from the source is the dominant transport mechanism. However, gas/water partitioning, aqueous solubility and the temporal evolution of VOC mixture composition control the extent of the gaseous phase plumes. For example, (i) the less volatile decane and 1,2,4-trimethylbenzene reach higher normalised concentrations at the sampling locations either at later times when their mole fraction has greatly increased or as a result of diffusion from the aqueous plume near the water table (Fig. I.3.4), (ii) concentrations for all mixture components in the lower permeability and higher water content soils (loam and silt) are higher than that of the sand except for benzene where, because of its higher aqueous solubility, mass transfer from the gas to aqueous phase act as a retardation mechanism to gaseous plume spreading; in the same soils, gaseous concentrations for decane are up to 1 order of magnitude higher than in sand due to the high Henry's law constant and low aqueous solubility (Fig. I.3.5).

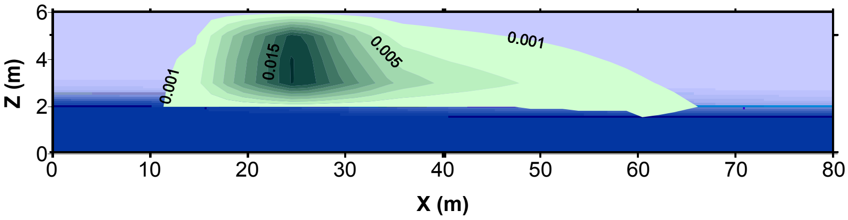


Figure I.3.4: *Normalised gaseous concentrations in sand of 1,2,4-trimethylbenzene at day 280.*

Biodegradation may greatly reduce the maximum gaseous concentrations of mixture components, especially those with greater aqueous solubility (i.e. benzene). Source location relative to the ground surface and the water table is an important factor affecting the spreading of the VOC plumes of the more volatile compounds in sand. In our case, placing the source zone 1 m closer to the water table results in concentrations about 1 order of magnitude higher than in base case for benzene, methylcyclopentane and pentane. However, the effect of source location is diminished for the least volatile components.

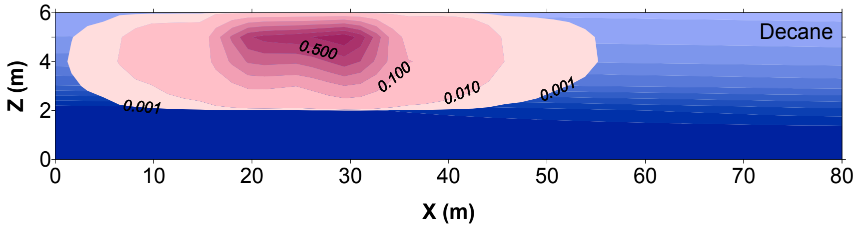


Figure I.3.5: *Normalised gaseous concentrations in silt of the decane at day 30.*

Time to depletion of each VOC mixture compound from a residual source

The time after which 80% of the mass (about 8 kg) of each compound of the VOC mixture is depleted from the source is given in Table I.3.2. The compounds with higher vapour pressure (i.e. pentane) are depleted from the source much faster than the less volatile mixture components. The time to depletion from the NAPL source increases (by more than one order of magnitude for the least volatiles) in less permeable soils with higher water content, as well as when recharge is incorporated, primarily due to reduced mass transfer rates to the atmosphere. Biodegradation may significantly reduce the time to depletion for all biodegradable compounds. High aqueous solubility enhances the effect of biodegradation on the time to depletion. For example, in our case, benzene is the first mixture compound to be depleted although it has lower vapour pressure and biodegradation rate than methylcyclopentane. Source location relative to the ground surface and the water table may be one of the most important factors affecting the time to depletion from the NAPL source of all VOC mixture compounds. Placing the source zone 1 m closer to the water table increases the depletion time of all compounds by more than one order of magnitude. The mixture composition could have a significant effect on the transport and fate of VOC components because it may alter the mole fraction temporal evolution of the individual compounds. The use of first order rate of 0.1 d^{-1} instead of equilibrium partitioning results in higher depletion times and lower maximum concentrations, however, the analogy of the relative effect of the various factors remain the same.

Table I.3.2: *Time (in days) after which 80% of mass (about 8 kg) of each compound in the residual source is depleted.*

NAPL	*Pentane*			*Methylcyclopentane*			*Benzene*			*1,2,4-TMB*			*Decane*		
Soil type	*sand*	*loam*	*silt*	*sand*	*loam*	*silt*	*sand*	*loam*	*silt*	*sand*	*loam*	*silt*	*sand*	*loam*	*silt*
BC	10	*15*	21	21	28	65	**33**	50	130	320	1120	3300	340	1140	3570
R	11	16	26	27	40	140	44	80	400	410	3400	4000	420	3430	4000
S,B	9	12	14	14	18	20	11	12	14	35	50	65	93	220	390
S,B,R	8	11	20	12	17	27	10	11	13	32	49	62	72	350	650
D_2	69	140	380	150	360	920	240	960	2560	3250	4000	4000	3600	4000	4000
C_2, BC							27	50	135	172	1050	3680			
Tr, BC	17			58			96			1260			1350		

Tr: Transfer rates of 0.1 d^{-1} are used instead of equilibrium partition among phases.

I.3.3 NAPL mixtures versus pure NAPLs

As shown in the above discussion, simulating the transport of complex NAPL mixtures is much more difficult compared to pure NAPLs. Even when mixture components do not chemically react with each other, mixture composition may have a profound effect on the transport of each individual constituent as described by Rault's Law for dissolution and volatilisation. Furthermore, mixture composition (mole fractions of the individual organics in the NAPL mixture) change with time due to different mass transfer rates from the NAPL phase to aqueous and gaseous phases. Also, the effects of hydrogeologic setting, different processes and different physical-chemical properties of the individual mixture components on the transport process are interrelated. Therefore, the use of a numerical code that incorporates at least the most important processes is considered essential for such studies.

As a general rule, modelling transport and fate of each mixture component separately, that is ignoring the potential effect of mixture composition on the transport process, will result in overestimating the maximum concentrations and spreading of gas and aqueous plumes in the vadose zone, as well as in underestimating the time to depletion of the simulated constituent from the NAPL source. However, there are cases that this approach can provide a good approximation of the transport behaviour of a single mixture component. Such cases are:

i. The properties of the simulated compound and the rest of the mixture components is of similar magnitude (mole fractions do not change considerably with time); in this case, the aqueous solubility and vapour pressure values assigned to the simulated compound should be multiplied with the mole fraction of the compound in the mixture.

ii. Vapour pressure of the simulated compound is at least one order of magnitude smaller than the rest of the mixture components; in this case, the effect of mixture composition on the transport of the simulated compound is very small since the residence time of this compound is much greater than the rest of the mixture components.

A major difficulty that is typically encountered when real contamination problems are studied is the large number of constituents in the actual VOC mixture compared to the number of species that can be handled numerically. Based on data from the EPFL lysimeter test, we developed a simplified approach to overcome this problem. It consists of simulating few mixture components (target contaminants) that represent the main threat of subsurface contamination as individual constituents while simulating the rest of the mixture hydrocarbons using a small number of pseudospecies (composite constituents). A methodology that is based on the minimisation of an objective function is introduced for selecting the optimal grouping criterion that minimises the uncertainty of model predictions, while the appropriate effective property values of the composite constituents in relation to the property values of the member hydrocarbons are identified. A detailed description of this approach can be found in Gaganis et al. (2002) (see appendix).

Lessons learnt and recommendations

Scenario specific modelling of spreading of VOC plumes:

✓ An **immobile VOC source near the ground surface results in gaseous and aqueous phase plumes with lateral exten**t in the order of few tens of meters.

✓ The **source location relative to the ground surface and the water table is a critical factor** affecting primarily the spreading of the VOC plumes of the more volatile compounds in low water content conditions (e.g. sand), which promote gas diffusion to the atmosphere.

✓ Compared to the case of a VOC source located at the ground surface, a **source a few meters deeper may result in an increase of subsurface contamination and time to source** depletion by more than one order of magnitude.

✓ **Biodegradation may reduce the maximum gaseous concentration of VOC** components and the time to source depletion by up to two or three orders of magnitude. The effect of biodegradation is more pronounced for VOCs with relatively high aqueous solubility (i.e. benzene) and less permeable soils with high water content. Biodegradation causes steeper concentration gradients resulting in faster volatilisation of compounds from the source.

✓ **Numerical modelling** of the GRACOS field experiments have shown that the **transport of VOC mixtures in the vadose zone** can be reasonably well addressed with relatively simple models when the following **minimum data requirements** regarding the dominant aspects of the problem are met:

(i) A **detailed characterisation of the hydrogeologic** conditions, especially the water content profile, water table elevation, groundwater velocity, soil permeability and recharge.
(ii) A **good knowledge of the location, the quantity, and the composition of the NAPL source.**
(iii) **Estimates of biodegradation rates** for the given soil and NAPL composition **from lab experiments**. See http://www.uni-tuebingen.de/gracos for animated results from numerical modelling.

I.4 Transport across the capillary fringe

Lead Authors: Dietrich Halm, Peter Grathwohl

I.4.1 Introduction

Once a volatile contaminant has entered the vadose soil zone the risk of contamination of the underlying groundwater has to be evaluated. Volatile contaminants spread in the vadose zone by gaseous diffusion and some of them vertically by advective transport in seepage water during groundwater recharge. Without degradation, they may reach the groundwater table and will be transported across the capillary fringe into the groundwater. Since transport phenomena in the capillary fringe are not completely understood we focus here on simple and practical approximations to estimate contaminant fluxes into the groundwater.

I.4.2 The capillary fringe

The capillary fringe represents the area between the vadose zone and the water table (saturated zone). It is defined as the zone, where surface tension forces hold the water against the atmospheric pressure. Pores within the capillary fringe are almost completely saturated with water. Contaminants can cause a lowering of surface tension compared to uncontaminated water, and this is expected to reduce the height of the capillary fringe. Hydraulic conductivity and horizontal movement of water within the capillary fringe is reduced by entrapped-migrating air bubbles. This difference of flow velocities between capillary fringe and underlying groundwater imposes a drag force on groundwater at the water table. Transversal movement of solutes in the capillary fringe takes place by molecular diffusion and in parts where the water is mobile via dispersion.

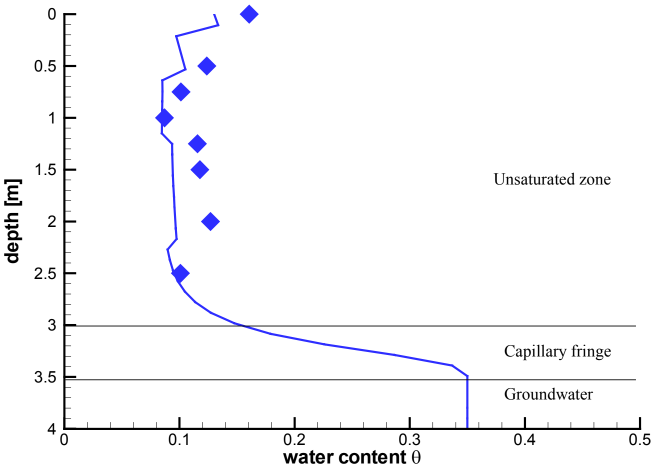


Figure I.4.1: *Increase of water saturation with depth from the unsaturated zone across the capillary fringe in a sandy soil at the GRACOS field site, Airbase Værløse (symbols: measured values by TDR, solid line: simulated).*

I.4.3 Mass transfer from soil gas to the groundwater

Two mechanisms can be responsible for groundwater contamination: (a) the diffusive/dispersive transport of volatile contaminants from soil-gas across the capillary fringe and (b) the advective transport of contaminants into the saturated zone by seepage water. Both cases can be treated as a boundary layer problem, i.e. by estimating the thickness of the layer of contaminated groundwater which forms below a contamination in the unsaturated zone. The aqueous concentration in this boundary layer C_w can be calculated from the gas phase contaminant concentration C_g and *Henry's law* constant H: $C_w = C_g/H$. For further details concerning theory and experimental validation of this approach see Klenk and Grathwohl (2002), Appendix 2.

Mass transfer by diffusion/dispersion across the capillary fringe

The flux from soil-gas to groundwater across the capillary fringe is usually dominated by dispersion and can be treated analogous to diffusion into a semi-infinite porous medium. The thickness of the boundary layer may be estimated based on the mean square displacement, which is a first approximation given by the square root of the product of transverse dispersivity (α_t) and length scale of contamination (x_{cont}), (see Fig. I.4.2).

Since transverse dispersivities are usually fairly low (i.e. < 1 mm) the thickness of such a layer is also very small (10 cm for $x_{cont} = 10$ m and α_t, =1 mm).

Mass transfer to groundwater: Recharge by percolating water

Water percolating down the soil-profile with small velocities (usually the mean annual recharge-rates are a few decimetres per year) is equilibrated with soil-gas. The thickness of a boundary layer due to infiltration of seepage water can be estimated in a first approximation from the mean annual groundwater recharge rate $v_{recharge}$ (e.g. 1 mm day^{-1}) divided by the porosity times the contact time of groundwater with the contaminated area (given by the length scale of contamination divided by the *Darcy velocity* of groundwater flow):

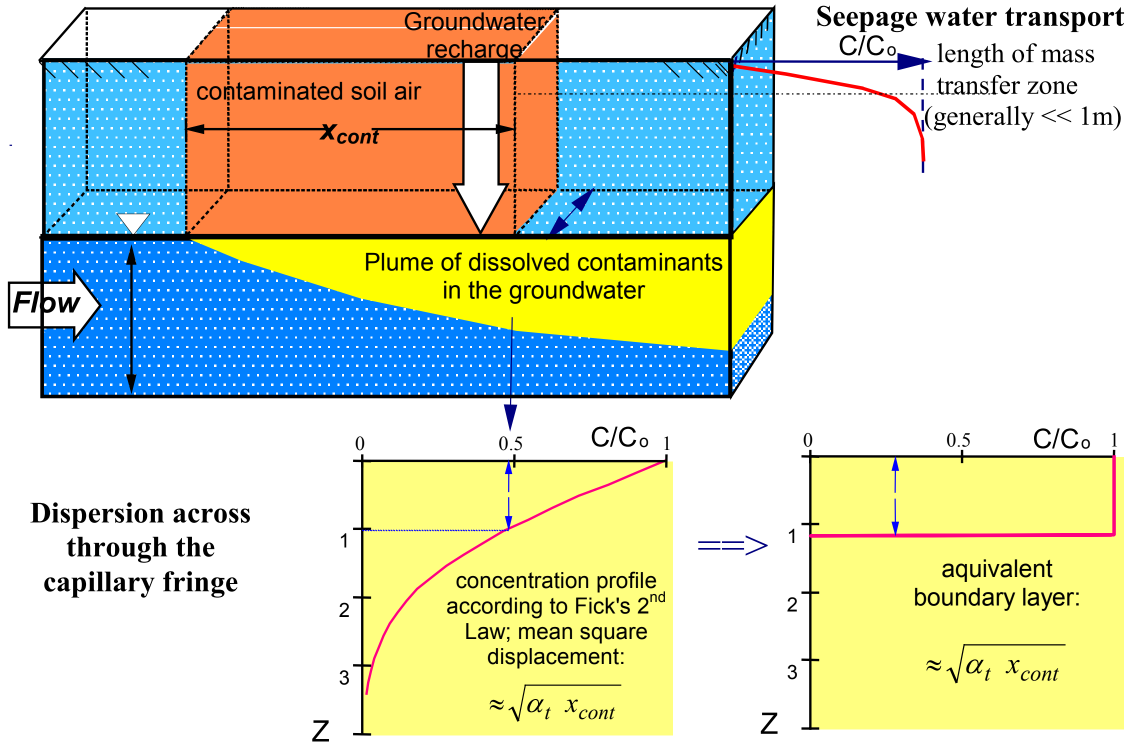


Figure I.4.2: *Conceptual model for mass transfer across the capillary fringe.*

I.4.4 Fluxes and concentrations in the groundwater

A main advantage of the boundary layer approach is that the contaminant fluxes into the groundwater can be easily calculated from the *Darcy velocity*, the lateral extent of the contaminated area (width) and the contamination concentration in the vapour phase at the capillary fringe.

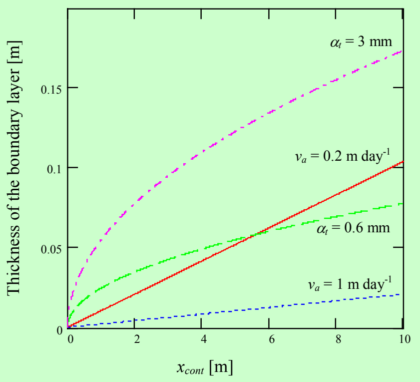
If the thickness of the boundary layer is known, then the contaminant flux into the groundwater F_{cont} can be calculated from the average groundwater flow velocity, the contaminated area, and the contaminant concentration in vapour phase divided by *Henry´s* law constant.

The depth-averaged concentration in groundwater can be easily calculated from the thickness of the aquifer h:

$$C_{groundwater} = \frac{C_g}{\mathrm{H}}\frac{z}{h},$$

with z/h representing a simple dilution factor.

Boundary layers from dispersion compared to groundwater recharge:



Boundary layers caused by dispersion of pollutants across the capillary fringe are significantly thicker than boundary layers which form from groundwater recharge. For this example groundwater recharge was set to 250 mm year^{-1}; the porosity was 33%. Only at small dispersivities (α_t = 0.6 mm) and slow flow velocities (0.2 m day^{-1}) the boundary layer originating from groundwater recharge becomes bigger than from dispersion if the length of the contaminated zone is longer than 6 m. Higher flow velocities and/or smaller groundwater recharge rates cause a proportional decrease of the thickness of the boundary layer. According to current theory the thickness of the dispersion related boundary layer is independent of the flow velocity if it is below 5 m day^{-1}. Typical transverse dispersivities measured in laboratory studies are typically less than 1 mm; effective dispersivities in the field may be significantly larger (cm). For more details see Klenk and Grathwohl (2002).

Lessons learnt and recommendations

Transport across the capillary fringe (see also Klenk and Grathwohl, 2002)

✓ The **capillary fringe** represents the area between the vadose zone and the saturated zone and is defined as the zone where surface tension forces hold the water against the atmospheric pressure.

✓ **Hydraulic conductivity and horizontal movement of water within the capillary fringe** is reduced by entrapped air bubbles.

✓ **Transversal transport of solutes in the capillary fringe** takes place by molecular diffusion and in parts where the water is mobile via dispersion.

✓ Two mechanisms contribute to groundwater contamination:
  - **Diffusive/dispersive transport** of volatile contaminants from soil-gas across the capillary fringe.
  - **Advective transport** of contaminants into the saturated zone by seepage water.

✓ Both cases can be treated as a **boundary layer problem**, i.e. by estimating the thickness of the layer of contaminated groundwater which forms below a contamination in the unsaturated zone.

✓ If the **thickness of the boundary layer** is known, then the **contaminant flux into the groundwater** F_{cont} can be calculated from the average groundwater flow velocity, the contaminated area, and the contaminant concentration in vapour phase divided by *Henry´s* law constant.

Part II Pollutant leaching from contaminated soil and other materials

II.1 Introduction/philosophy/questions to be addressed

Lead Authors: Hans van der Sloot, Rob Comans

All over Europe, numerous contaminated sites exist where top layers of soil or other materials are contaminated. Full remediation will be economically impossible apart from the fact that in many situations the total composition may be increased relative to natural soil composition, but at the same time the risk to subsoil and groundwater may be minimal. Judgement based on leaching is more appropriate to assess long-term impact from contaminated sites than evaluations based on total composition.

For release of inorganic and organic constituents (major, minor and trace elements) from contaminated materials into water, it is important to identify a few key issues. These relate to:

- the nature of the constituents of concern, which may have very different release behaviour based on their chemistry and the local conditions
- the major release mechanism in soil and soil like materials, which will be usually percolation dominated. This then points as percolation based testing protocols for assessing release.
- the hydrology of the site under consideration, i.e. how much infiltration will occur and what are the relevant/preferential flow paths.
- the nature of the contamination source in terms of release controlling parameters such as pH, EC, redox and dissolved organic matter (DOC)
- the changes in release conditions with time due to processes such as depletion of source material, changes in main release controlling parameters and changes in permeability due to pore clogging.
- the behaviour of released constituents in the subsoil and in groundwater
- the targets to be evaluated in the consideration of acceptance or rejection and subsequent requirement for mitigating measures up to full remediation.

Several questions may need to be answered in a site evaluation. Preferably such questions can be answered with the same type of characterisation data. In ENV 12920 (CEN/TC292/WG6, 1999), a number of steps have been identified, which help address the information needed to answer a specific question. In the following, an evaluation of soil and soil like material will be addressed that provides answers to questions such as those listed below.

Question posed may be:

- How can a given contaminated site be evaluated?
- What parameters should be used to evaluate such a site?
- What type of sampling should be followed to assess potential impact?
- What tests are applicable to evaluate the site?
- Will significant changes in release occur over time?
- Is the material contaminating the site biodegradable?
- What are the possibilities for natural attenuation?
- What are the main contaminants that potentially cause a problem?
- What is the risk that the contaminated site will impact subsurface/groundwater?
- What is the risk that the contaminated site leads to plant uptake and human exposure by inhalation/ingestion?
- How long will it take for the site to show measurable impact in subsurface/groundwater?
- Should the contaminated site under consideration be remediated?
- What is the impact will result from remediation?

- What type of remediation could be applied?
- How do remediation options compare?
- What is the risk to subsurface/groundwater after remediation?
- How to evaluate the remediation endpoint?
- What are the main parameters to follow for long term monitoring?
- If no action is taken, where and how often should monitoring be done?

Almost all of these questions can be traced back to a quantification of the release and/or concentration of inorganic and organic contaminants in the aqueous phase at a specified point of compliance. A suitable combination of (characterisation) leaching tests and models, as described below, provide the necessary instruments.

In Fig. II.1.1, a schematic representation is given of a contaminated site, where process, influencing factors and targets are illustrated. A major distinction can be made between the source term and means to assess the release to the subsoil as a function of time under the influence of varying controlling factors with time and the transport of contaminants from the boundary of the site to subsoil and groundwater to an identified target. Modelling is a key aspect in both describing a time-dependent source term as well as in quantifying the transport of contaminants through soil and groundwater. The latter part of the evaluation can be made site specific by taking into account different flow regimes and retention characteristics of the subsoil or it can be made in a more generic manner using default values with relatively conservative estimates for flow and retention. There is an important difference between the source term description and transport behaviour at a chosen site. This is also related to the fact that, if ex-situ remediation will be required, the characteristics of the source are more important than the properties of the surroundings. In the following discussion, these aspects are separated. Finally, a relationship between laboratory and field verification is crucial to adding credibility to the testing and modelling efforts.

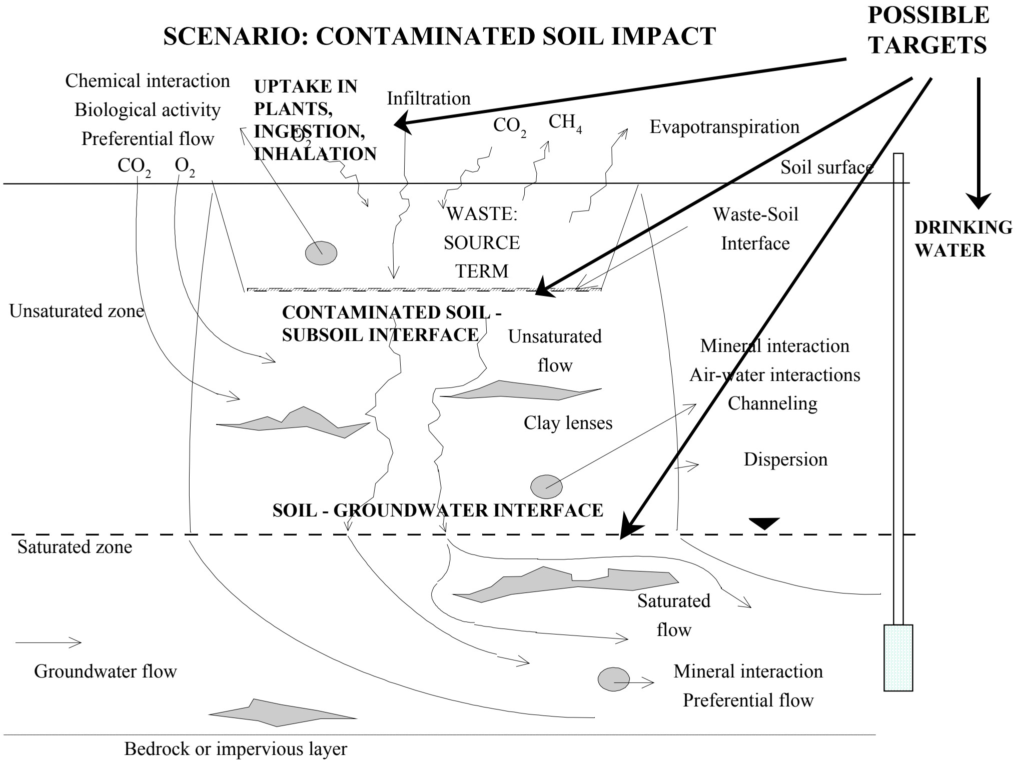


Figure II.1.1: *Schematic representation of a contaminated site with relevant targets for judgement.*

The aim of leaching tests is to determine the expected contaminant concentration in water as it percolates a sample specimen. Critical parameters in leaching tests are the contact time and the mass transfer rate into the aqueous phase. Extended contact times result in equilibrium conditions between the solid phase and the water, bringing further mass transfer to an end. Equilibrium concentrations may depend on additional dissolved matter. In the case of non-ionic organic contaminants these are for example dissolved organic matter and colloids. For heavy metals aditionally pH and redox conditions play an important role. Standard batch tests may show a reduced equilibrium concentration due to higher dilution as the solid/liquid ratio is increased. Otherwise equilibrium concentrations can be considered as the maximum concentrations (‘worst case’ scenario), which, due to time limitations are not always encountered in laboratory tests or under certain field conditions, if release kinetics are limiting.

Sampling is a relevant issue, that has not been covered extensively in this work. In other studies (i.e. project HORIZONTAL (www.ecn.nl/library/horizontal)) sampling of soil, sludge and biowaste is addressed and standards are developed to be adopted by CEN. In CEN TC 292 sampling standards are developed for many different modes of sampling (pile, conveyor belt, etc.). Documentation of integrated testing and judgement is currently in discussion in CEN/TC 292.

II.1.1 Total versus potentially leachable and actual leached amounts

Total composition is inadequate for environmental assessment purposes, as for many constituents a significant fraction of the total content is essentially non-leachable by water. A key aspect to judge the risk, that contaminated sites may pose, is the release to the water phase. This can be subdivided in potentially leachable, which is a maximum amount leached under predefined worst-case conditions, and in actual leached amount, which is the amount leached under the conditions imposed by the material itself. In Fig. II.1.2 the leaching behaviour of Cd from a heavily sewage sludge contaminated soil is given as an illustration. The possible uses of leaching test data to assess impact at specified targets is indicated. The aspects relating to plant uptake and human exposure in the form of ingestion or inhalation is not discussed here further. However, the test methods such as the pH dependence test (see section II.2 below) do allow such judgements. Fig. II.1.2 also illustrates that other test methods can be placed in perspective to one another by plotting such test data as a function of pH. This even applies to the test data obtained from sequential chemical extraction schemes, provided the data are calculated as cumulative leached amounts in subsequent leaching steps. It is recommended that site evaluation is based on leaching rather than on total composition analysis, which is currently employed in regulation. The advantage of judgement based on leaching versus total composition is that the assessment is taking place on true aspects causing environmental impact. Essentially non-leachable constituents can then not cause confusion and controversy as they will not show up in a leaching test.

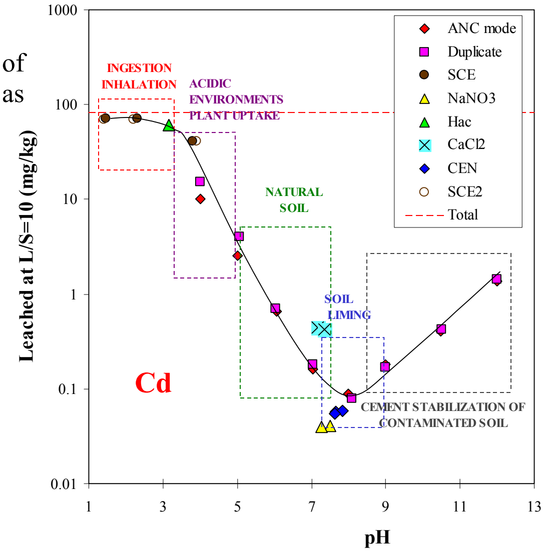
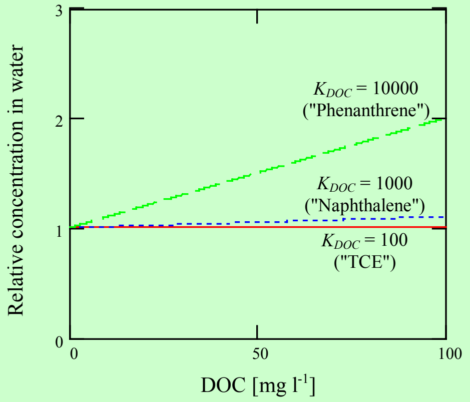


Figure II.1.2: *Relevant pH domains for assessing different questions in relation to different types of impact (L/S: Liquid/solid ratio) .*

Influence of dissolved organic carbon (DOC) compounds:



A significant influence of DOC (> factor 1,5) appears only for highly hydrophobic compounds (K_{doc} > 10000, e.g. 3ring PAHS) and DOC concentrations above 50 mg l^{-1}. K_{DOC}s of 100, 1000 and 10000 would be roughly representative for Trichloroethene (TCE), Naphthalene and Phenanthrene, respectively.

II.1.2 Source term description using leaching tests

Many factors that influence release of inorganic contaminants from a contaminated site can be assessed through leaching tests. Although a wide variety of leaching tests is available in literature, only a limited set of tests suffices to address key processes and influencing factors in by far most cases. For a largely percolation dominated situation at a contaminated site, a percolation test is the most crucial test to evaluate the risk of groundwater contamination. In case of rather impermeable materials (e.g. clay or clayey material) a compacted granular leach test has been developed that addresses diffusion controlled release from granular materials, that in a given scenario behave more like a flow-around “monolith” than as granular percolating material. In addition to the liquid to solid ratio (L/S) dependent release behaviour as obtained in a percolation test, a pH dependent leaching test provides information on the chemical speciation of the contaminated soil material, which is crucial for assessing the release under changing conditions of pH, EC, redox and dissolved organic carbon (DOC) level in leachate. For the projection to long-term, modelling is important as laboratory testing, medium scale and even full scale testing cover only a limited time-span relative to the time-frame over which answers are sought. Based on many years of experience a database/expert system has been developed (section II.6), which couples laboratory test data, physical aspects of release (hydrology), chemical changes in material properties with time and chemical reaction / transport modelling.

Lessons learnt and recommendations

Introduction/philosophy/questions to be adressed:

✓ A major distinction has to be made between the **source term** where the aqueous leaching takes place and **the transport of pollutants in the subsoil** to the groundwater as a function of time under the influence of varying controlling factors.

✓ Total contaminant content is inadequate for environmental assessment purposes, as **for many constituents a significant fraction of the total content is essentially non-leachable**. A **key aspect** to judge the risk, that contaminated sites may pose, is the **release to the water phase**.

✓ **Column leaching tests** are an important laboratory tool commonly used for the **determination of desorption or dissolution rates of (mobile) contaminants from various materials** (e.g. contaminated soils and sediments, construction materials, demolition waste etc.) which can be an important contaminant source for groundwater pollution when they are deposited above (e.g. artificial fillings in the unsaturated zone) or below the groundwater table (e.g. construction components in the saturated zone).

✓ **Critical parameters** in leaching tests are the **contact time and the mass transfer rate into the aqueous phase**. Extended contact times result in equilibrium conditions between the solid phase and the water. Equilibrium concentrations may depend additionally on dissolved matter. In the case of non-ionic organic contaminants these are for example dissolved organic matter and colloids, whereas for heavy metals pH and redox conditions play an important role.

✓ In case of rather **impermeable materials** (e.g. clay or clayey material) compacted **granular leaching tests** have been developed which address the diffusion controlled release from granular materials, which in a given scenario behave more like a flow-around “monolith” than as granular percolating material.

✓ **pH-dependent leaching tests** provide information on the chemical speciation of the contaminated soil material, which is crucial for assessing the release under changing conditions of pH, EC, redox and dissolved organic carbon (DOC) level in leachate.

✓ **Modelling is a key aspect** in both describing a time-dependent source term as well as in quantifying the transport of contaminants through soil and groundwater.

II.2 Leaching test methods

In the literature a large number of leaching tests are described. However a limited number of well-selected methods will suffice to address release from many different materials (Fig. II.1.2. and II.2.2). Two main aspects need to be addressed in testing: chemical speciation (pH, redox, DOC, etc) and time-dependent release. An additional distinction in methods applicable for granular materials (percolation dominated regimes) and for monolithic materials (diffusion dominated and/or surface area related release) is crucial (Harmonisation of leaching tests, 1997). Finally, a distinction in characterisation tests and compliance tests for quality control purposes is important, as relatively quick to perform tests suffice when a material or material class has been sufficiently characterised. Several of these methods have already been standardised at European level through CEN (European standardisation body).In addition to these leaching test methods, a limited number of additional methods are needed to quantify specific parameters for modelling purposes, such as selective chemical extractions (sorption/binding parameters for Fe-, Al- and Mn-(hydr)oxide and particulate and dissolved organic matter).

Relevant standardisation activities in CEN and ISO

CEN/TC292:

- WG2 EN 12457 1– 4 Granular waste compliance leaching test - validated
- WG2 – Monolith compliance leaching test – Tank leach test 3 days (draft for enquiry)
- WG6 – pH dependence leaching test Pr EN 14429 – 2003 for formal vote
- WG6 – percolation test PrEn 14405 – 2003 for formal vote
- WG6 – NWIP Dynamic monolith leach test (similar to NEN 7345)

ISO/TC 190:

- SC7 WG6: Batch leaching tests at L/S=2 and L/S□ and percolation test for soil materials (based on CEN TC 292 procedures)

A short description of the methods is provided in Appendix A6.

Example: To illustrate the relationship between the different characterisation tests and the compliance test for granular materials, Fig. II.2.3 shows the leaching behaviour of Cu from two contaminated soils. In the left hand graph, data from the pH dependence leaching test are shown, which give information on the chemical speciation of the elements. The compliance tests data as obtained in the European EN 12457-2 are inserted to show the consistency of EN 12457-3 data with the characterisation test data. In the right hand graph, leaching data from the percolation test are shown as cumulative release vs. the liquid/solid (L/S) ratio (in l/kg). In this graph, the EN 12457-3 data are also inserted. The shape of the curve gives information on the release behaviour; the slope of ~ 1 indicates that Cu is leached in a largely solubility-controlled fashion.

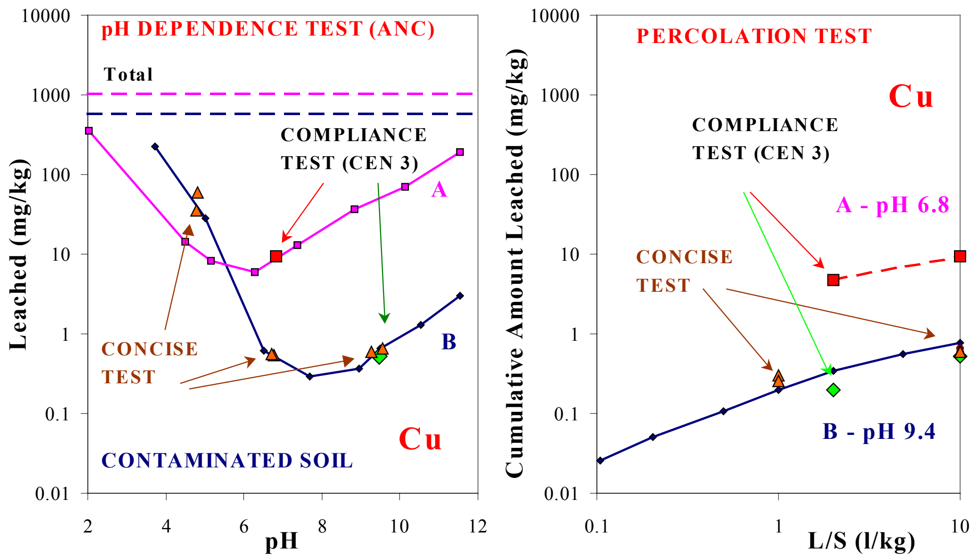


Figure II.2.1: *pH dependence leaching tests data and percolation test data for two contaminated soils (A and B) in comparison with compliance leaching tests data (EN 12457-3) and a concise test.*

Interrelation of test data

The combination of the pH dependence leaching test and the percolation test with an identification of the release controlling mechanism at different liquid/solid ratios (as illustrated in the above example) holds the key to the interpretation of test results. With the information from these two tests, a reasonable estimate of release can be derived for conditions which have not been tested or which only occur at the long term. Very large differences (factors 10 to 1000) can occur in contaminant release under changing environmental conditions (pH change, redox change, change in EC or change in DOC). Therefore, it is important to be able to estimate such changes with a reasonable degree of certainty rather than to rely on inadequate test data which do not allow for predictions of release at conditions beyond those applied in that specific leaching test. For many constituents the leaching behaviour is such that predictions can be made with fairly good precision. Examples are very mobile species, such as elements or constituents that do not react appreciably with the matrix. Another group is formed by elements or constituents that are clearly solubility-controlled over the relevant L/S and pH-range under consideration. Although further model-development is needed, a full integration of test data from well-designed experimental work (i.e. the above mentioned prEN14429 and prEN14405 tests) with geo-chemical modelling can already significantly improve predictions of release at the long term, than is currently possible based on single regulatory test data or non-interpreted characterisation test results. Below several individual aspects will be addressed that already can be taken into account.

Hierarchy in testing: use of simplified vs. sophisticated (characterisation) tests

For quality control purposes relatively quick procedures are needed providing as much information as possible. A hierarchy in test use is promoted, in which more sophisticated tests are used for development of regulation and development of treatment options, whereas for quality control in material processing or quality variations within a specific source of material more simplified tests are used. The tests mentioned before like EN 14405 and 14429 are typical characterisation leaching tests. The next level of test is the concise leaching test (Kosson et al, 1997). It consists of 4 extractions, of which two at native (not adjusted) pH using a low (L/S=1) and a high L/S (L/S=10) and two extractions at L/S=10 at controlled pH using a low pH to assess availability and a higher pH to assess the sensitivity to DOC mobilisation, pH change by external factors and increased anion mobility. A key aspect in this test is the mandatory measurement of pH, EC, redox potential and DOC in all extracts. When more information is available, one of these extractions may be sufficient to judge the material behaviour (see Kosson et al., 1997 and Appendix A.6 for more information). It is advisable to assess a contaminated site by characterisation leaching tests using a representative mixture of samples from the site and subsequently evaluate the spatial variability by the simplified test protocols. The data from the simplified test can then be placed in perspective to the more extended information thus allowing further reaching conclusions than can be obtained from the simplified testing alone.

Relation between liquid/solid ratio (L/S) and time; testing at different scale

The relationship between infiltration, time and L/S has been evaluated in relatively simple terms by using the density, the height of the application and the net infiltration as parameters. As a first approximation, this is a useful means of comparing laboratory test data with medium- and full-scale test data. This aspect is illustrated in Fig. II.2.2 for a study of a sustainable landfill concept for predominantly inorganic waste. The consistency in the data from such very different scale experiments is very promising. The relationship takes the form:

$$L/S = (N*t)/(d*h)$$

with N the infiltration rate in mm/year, t the time in years, d the bulk density in kg m^{-3} and h the height of the contamination in m. The consistency of the data from different scales of testing indicates that laboratory data are of great value. In addition, Fig. II.2.2 shows that appropriate sampling and mixing of samples to constitute a representative mix apparently leads to more meaningful results than the often reported scattered data from individual sub samples constituting the waste mixture.

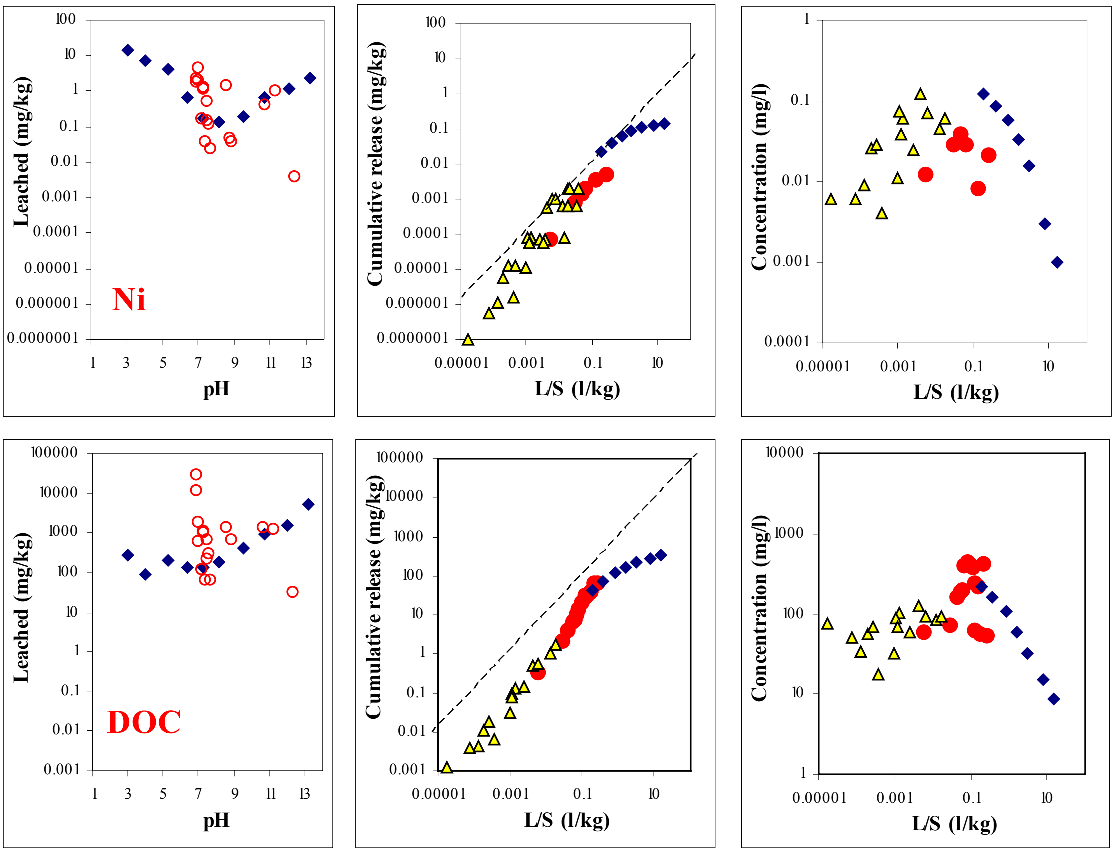


Figure II.2.2: *Relationships between pH dependence and percolation test (laboratory) for a mixture of wastes (integral mix, black diamonds) disposed in a 12,000 m^3 pilot cell with leachate data from individual wastes (open diamonds) and from 1.5 m^3 lysimeters (triangles) and the full scale pilot (filled circles). For more information see Appendix 6.*

Lessons learnt and recommendations

Leaching test methods

✓ A distinction in methods applicable for **granular materials** (percolation dominated regimes) and for monolithic materials (diffusion dominated and/or surface area related release) is crucial.

✓ Leaching test methods need to address two main aspects: **Chemical speciation** (pH, redox, DOC, etc) and time-dependent release.

✓ A **distinction in characterisation tests and compliance tests** for quality control purposes is important, as relatively quick to perform tests suffice when a material or material class has already been sufficiently characterised.

II.3 Leaching processes of heavy metals – inorganic constituents

Lead Authors: Hans van der Sloot, Rob Comans

II.3.1 pH-buffering; acid neutralisation capacity

The acid neutralisation capacity (ANC) as obtained from the pH dependence leaching test (PrEN14429) is a crucial parameter as it gives information on how much acid or base from external sources it takes to significantly change the native pH of a material. For example, in case of a soil that has in the past been highly amended with sewage sludge, a significant amount of its neutralisation capacity has been consumed, such that a limited change in external conditions (e.g. acid rain) may lead to a significant increase in metal leachability, as illustrated in Fig. II.3.1. Soils contaminated with alkaline materials (e.g. cement/concrete) will change in pH with time and the time it takes for such soils to become neutral can be derived from the availability of external neutralising sources, such as atmospheric CO_2, and biodegradation-derived CO_2 present in the soil gas. The rate of change is obviously very site specific and needs to be evaluated on a case by case basis.

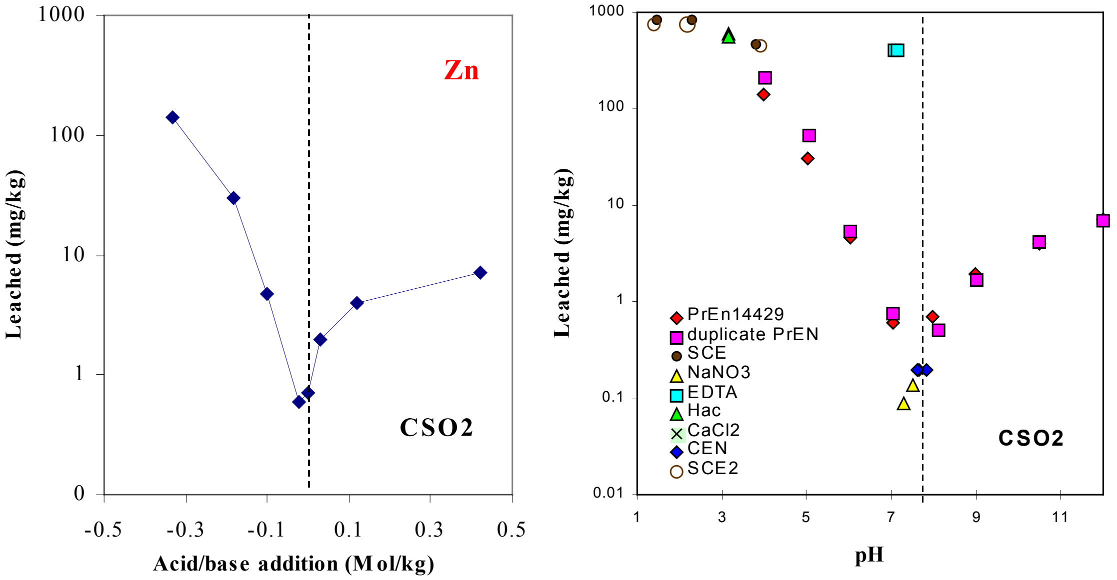


Figure II.3.1: *Sensitivity of metal release to a minor pH change due to external causes.* Left*: PrEN 14429 test data as a function of the acid/base neutralisation capacity of the soil (= resistance to pH change);* Right*: comparison of different tests in relation to pH dependence test (PrEN 14429) results. SCE: sequential chemical extraction data (cumulative at end pH of each extraction); SCE2:duplicate SCE test; NaNO3, CaCl2: mild water extractions; EDTA, Hac: Availability type extractions; CEN: EN 12457 demineralised water extraction.*

II.3.2 Facilitated leaching of heavy metals by DOC

The presence of dissolved organic carbon (DOC) has been shown to be a crucial parameter in almost any soil type. From mixing experiments of compost with MSWI bottom ash, it has been possible to quantify the effect of Cu mobilisation by complexation with DOC. In Fig. II.3.2 the effect of even very small amounts of DOC derived from compost on the mobilisation of Cu from MSWI bottom ash is illustrated. It is clear that upon addition of 1 % compost (which may simulate the use of MSWI bottom ash on an organic-rich soil or MSWI covered with a layer of top-soil) already a more than an order of magnitude increase in Cu leachability occurs. The data for increased DOC levels follow a consistent pattern of increased Cu leachability. The decrease of Cu leachability at low pH is related to the increased binding to particulate organic matter.

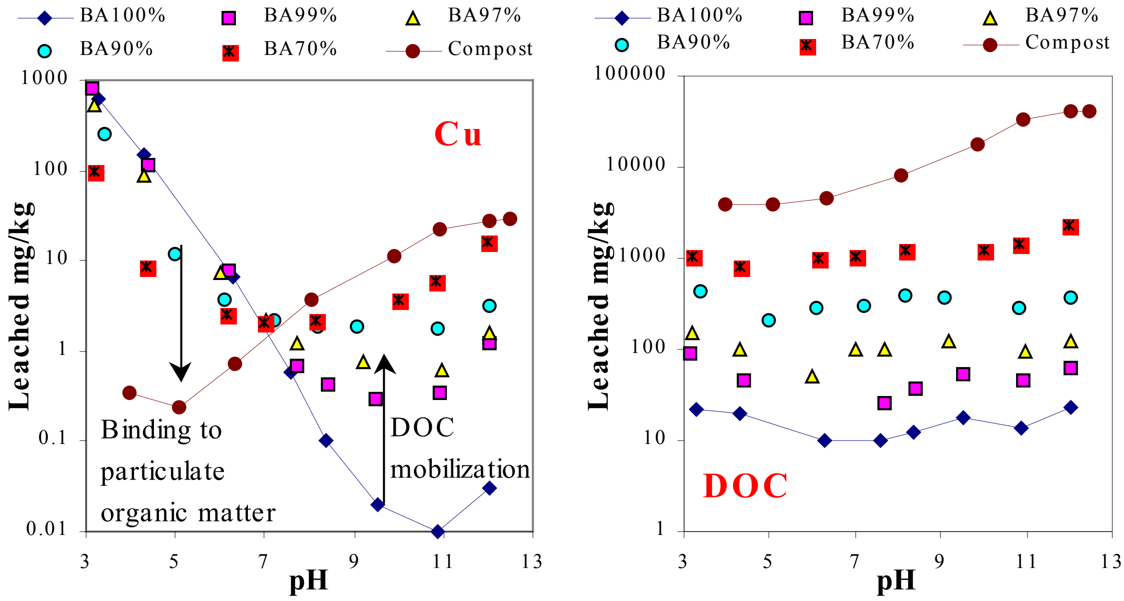


Figure II.3.2: *Mobilisation of Cu from a mixture of previously heated MSWI bottom ash (0 % organic matter) and compost in mixing proportions of 1, 3, 10 and 30 % of compost addition.*

II.3.3 Changes in redox potential with time

The effect of changes in redox potential (Eh) on contaminant release is as yet the least well documented, because it is rather complicated to control redox in a normal laboratory setting. Some experimental systems have been developed, but these are scarce. The role of reducing conditions can be substantial. In Fig. II.3.3 this is illustrated by the leaching of Ba from steel slag, which is markedly different in oxidised (solubility-control by $BaSO_4$) or reduced (no solubility-control because of sulphate reduction) conditions.

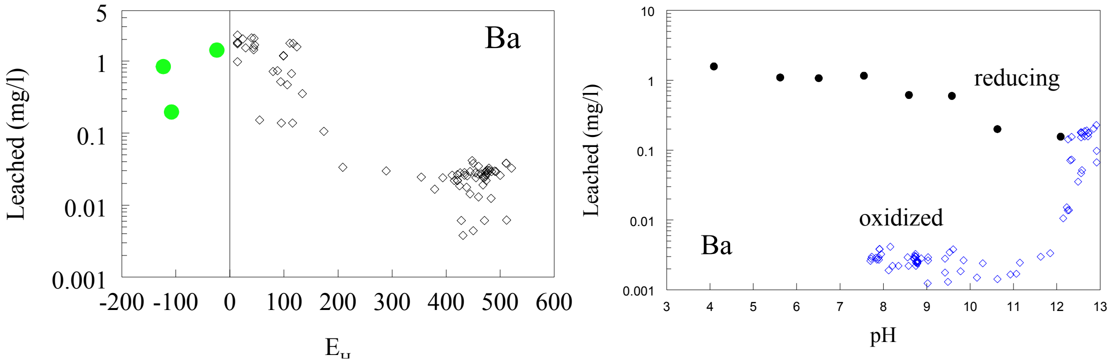


Figure II.3.3: *Leaching of Ba from steel slag as a function of pH under oxidised and reducing conditions.*

However, under (mildly) reducing conditions, DOC may still play a significant role in metal mobilisation. This effect is often neglected. In case of iron in reducing MSW landfills, this misconception has been illustrated by modelling Fe leachability (see Fig. II.3.4).

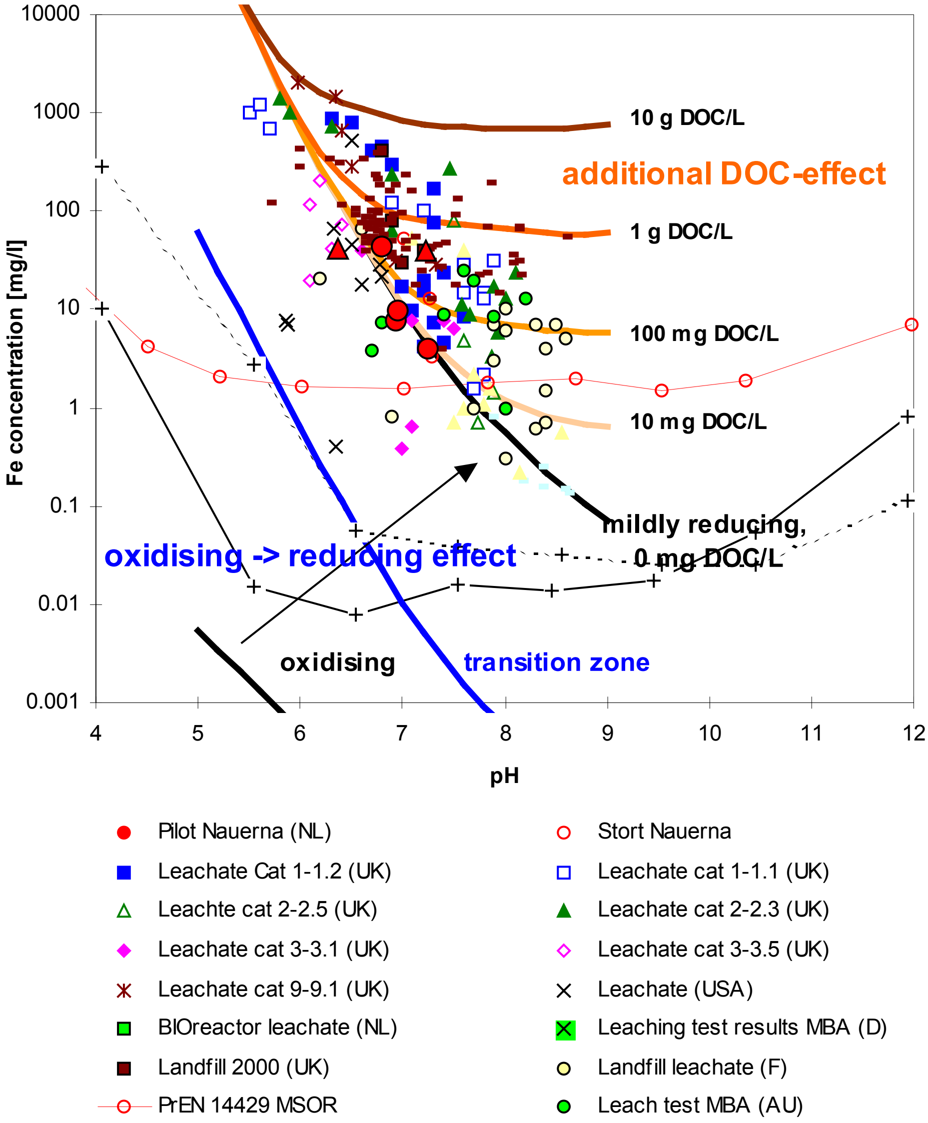


Figure II.3.4: *Results of modelling iron solubility in landfills with ECOSAT. Solid lines are model output. The arrow at the bottom of the figure indicates the effect of only redox conditions (DOC = 0 mg/L) when going from an oxidised system to a reduced system. The large red dots in the centre of the picture are data from the pilot predominantly inorganic waste landfill at Nauerna. The triangles are from the corresponding laboratory tests. Samples illustrated come from: Pilot Nauerna: Predominantly inorganic waste landfill Nauernasche polder (NL), UK landfill data: Category 1 – 9 Landfill leachate (Robinson et al); Army Creek Landfill (USA); Bioreactor leachate – Leachate from Bioreactor pilot study at VAM (now ESSENT) Netherlands; Leaching test MBA (D) – leaching test data for MBA rest product – Germany; Landfill 2000 – Leachate data from pilot study Landfill 2000 in the UK; Landfill leachate France – Data from different landfill sites in France (Sardinia Conference paper); MSOR: pH dependence leaching test results for Organic fraction mechanically separated from MSW prior to incineration; Leach test MBA (AU) – Leaching test data on different samples of biodegraded MSW - Austria.*

Chemical speciation modelling

The information from any type of leachate or aqueous solution for which the relevant data are available can be used to calculate the chemical speciation of the contaminants. From this type of modelling, information can be obtained on the relevant solubility-controlling phases, the importance of DOC for complexation, contaminant speciation and potential toxicity, etc. In Fig. II.3.5 the geo-chemical speciation is presented for Zn and Ba from a number of river and marine sediments. This includes identified mineral phases as well as metal-DOC association as function of pH. By applying speciation modelling to eluates covering a wide range of L/S and pH conditions, differences in relevant solubility controlling mineral phases may occur .

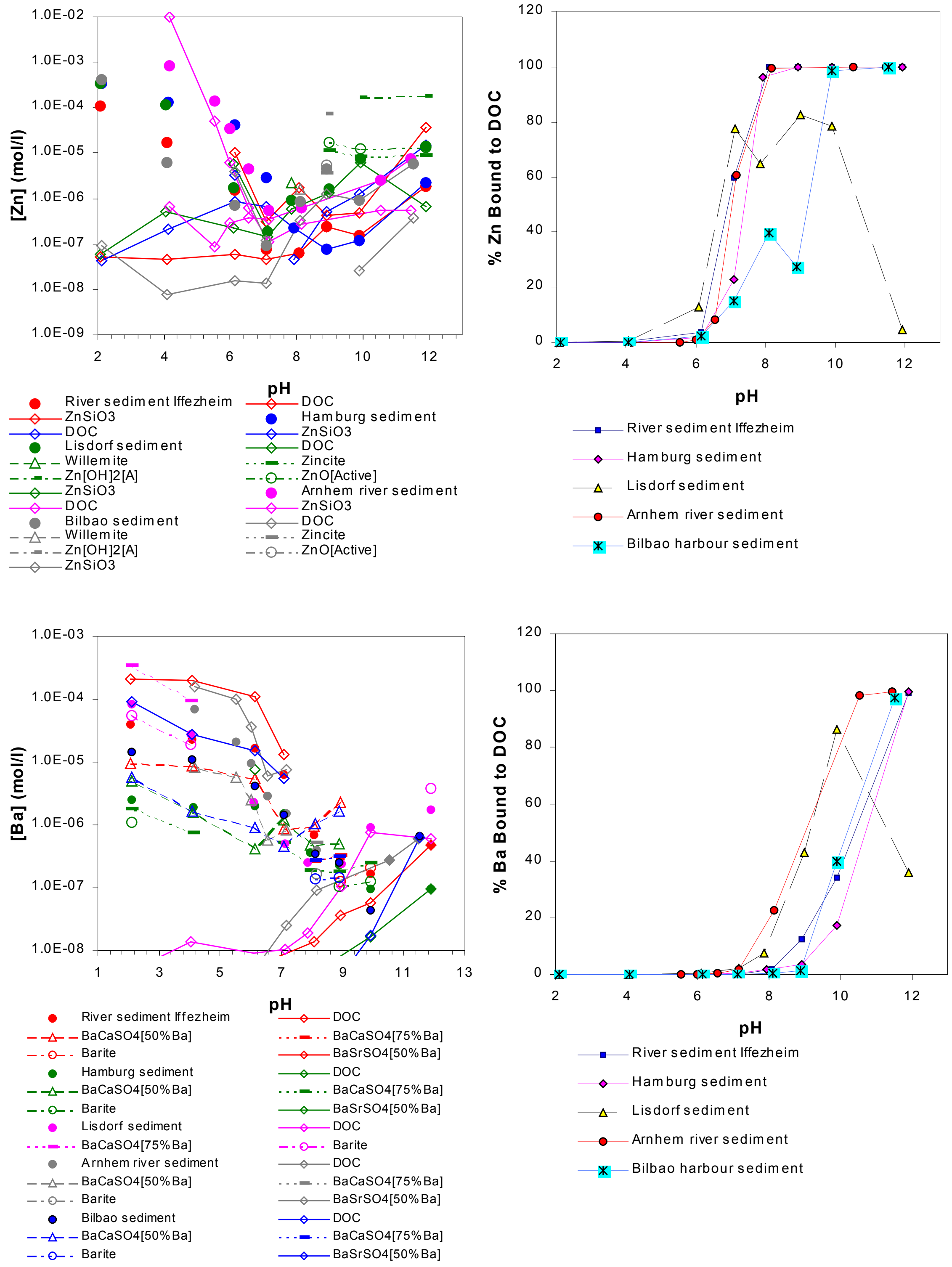


Figure II.3.5: *Geo-chemical modelling of Zn and Ba speciation in river and marine sediments, illustrating solubility controlling mineral phases and the element-DOC association.*

At low L/S (initial field condition) other phases may prove important, which upon further percolation will be replaced by others. Modelling pH dependence test data and at least one low L/S condition (L/S = 0.5 - 1) from a percolation test, is therefore crucial in addition to the modelling of pH dependence test results.

In Fig. II.3.6 this is illustrated for Zn leaching from two contaminated soils. The results of the modeling are given in comparison with the original data from the pH dependence leaching test and percolation test for these two soils. From the percent association of Zn with DOC as calculated from the modeling in both pH dependence test and percolation test, the association of Zn with DOC can be judged as very prominent. The integrated testing and modelling approach reflected by the graphical presentation in Fig. II.3.6 covers a very wide range of possible questions on utilisation, treatment, exposure and disposal as identified in section II.1. Recent work on organic contaminant leaching in the framework of the development of sustainable landfill concepts has shown that a similar approach is quite feasible for organic contaminants as well.

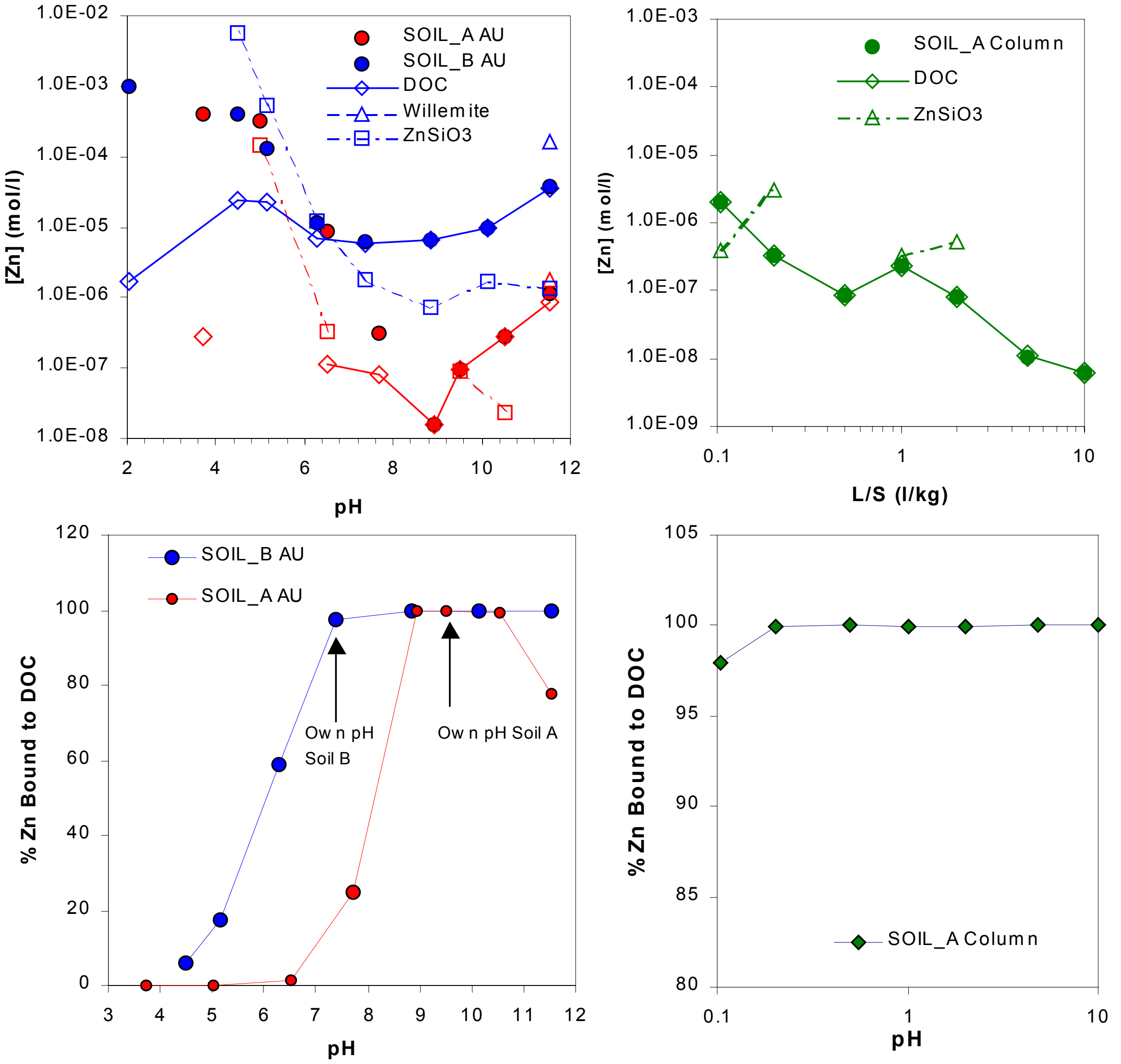


Figure II.3.6: *Modelling results of metal -DOC interaction using the NICA-Donnan model in ORCHESTRA for contaminated soils tested by pH dependence and percolation test showing potential mineral and Zn-DOC association as controlling factors. The percent association of Zn with DOC is given as function of pH and as function of L/S.*

Lessons learnt and recommendations

Leaching processes of heavy metals – inorganic constituents

- ✓ The **acid neutralisation capacity (ANC)** as obtained from the pH dependence leaching tests is a crucial parameter as it gives information on how much acid or base from external sources it takes to significantly change the native pH of a material.
- ✓ The **presence of dissolved organic carbon (DOC)** has been shown to be a crucial parameter that facilitates metal mobility in almost any soil type. Even under reducing conditions, DOC still may play a significant role in metal mobilisation.
- ✓ **Changes in redox potential (Eh)** may effect contaminant leaching by orders of magnitude. This is however not as well documented as e.g. the presence of DOC for it is rather complicated to control redox in a normal laboratory setting.
- ✓ From **chemical speciation modelling**, information can be obtained on the relevant solubility-controlling phases, the importance of DOC for complexation, contaminant speciation, potential toxicity, etc.
- ✓ The **integrated leaching behaviour** as reflected by the combination of the pH dependence leaching test data and the percolation test data can cover many different aspects relevant for the judgement of contaminated soils, sediments and waste materials in a variety of utilisation and exposure conditions.

II.4 Contaminated release from complex organic mixtures: Prediction of ageing behaviour

Lead Authors: Sayonara Brederode Ferreira Reckhorn, Peter Grathwohl

II.4.1 Introduction

Groundwater contaminations due to complex organic mixtures such as coal tar, creosote and fuels are a widespread problem in industrialised regions. Although most compounds in these mixtures are biodegradable, the contaminant sources are very persistent over many decades after the contamination occurred (e.g., more than 100 years ago at gasworks sites).

Generally two contamination scenarios types can be distinguished: 1) pools of organic phases of a DNAPL phase encounters low permeability domains in the subsurface and 2) residual NAPL saturation (e.g. > 3 % - 5 %) trapped in an aquifer as NAPL-blobs and ganglia.

II.4.2 Complex Mixtures and Raoult’s Law

In complex mixtures of organic compounds (e.g. coal tar, gasoline or diesel fuel), the aqueous saturation concentration ($C_{i,sat}$) of an individual component *i* depends on the composition of the mixture and is always less than the solubility of the pure substance in water. It can be determined in a first approximation from the fraction of the compound in the organic mixture ($f_{i,o}$) and its water solubility (S):

$$C_{i,sat} \approx f_{i,o}\, S_i$$

For a more precise determination of $C_{i,sat}$ *Raoult´s* law has to be applied (i.e. instead of $f_{i,o}$ the molar fraction $\chi_{i,o}$ has to be used, which equals $f_{i,o}$ only in case the molecular weight of the mixture is the same as for the compound. Additionally, an activity coefficient has to be introduced in order to account for non-ideal conditions: $C_{i,sat} = \chi_{i,o}\, \gamma_{i,o}\, S_i$). For compounds which in their pure state are solids (crystals) under ambient temperature and pressure the sub-cooled liquid solubility has to be used.

II.4.3 Dissolution of NAPL from zones of residual concentrations

At sufficiently high residual NAPL saturation (e.g. > 3 % - 5 %) the dissolution of NAPL-blobs and ganglia takes place under equilibrium conditions even within short flow distances along the flow direction. Fast dissolution kinetics have been confirmed in column experiments where the length of the mass transfer zone in general is less than 10cm (see Eberhard and Grathwohl, 2002). If the zone containing residual NAPL is much longer than that, then the dissolution time scale in a first approximation can be calculated based on the local equilibrium assumption. In this case $C_{i,sat}$ will be observed downstream of the smear zone for an extended period of time depending on the length of the smear zone. In a leaching test, this behaviour would be referred to as "solubility controlled" (linear increase of contamination is released with time).

The minimum time for removal of a NAPL constituent can be estimated from the velocity of the dissolution front of compound *i*, which is retarded compared to the groundwater. The retardation factor of the dissolution front is given by the ratio of the overall mass of contaminant present in the porous medium to the mass of mobile (i.e. dissolved) contaminant:

$$R_i = \frac{n}{n_e} + \frac{\rho_o f_{i,o}\, n\, S°}{C_{i,sat}\, n_e} \cong \frac{\rho_o S°}{S_i}$$

where ρ_o, n, n_e, and $S°$ denote the density of the NAPL (M L^{-3}), the porosity, the effective porosity (which is smaller than n by the NAPL-filled fraction), and the degree of NAPL saturation, respectively.

II.4.4 Dissolution from NAPL pools

The concentration profile which develops in the groundwater perpendicular to the flow direction above the pool can be calculated based on the analytical solution of *Fick's 2nd* law for diffusion into a semi-infinite porous medium and a constant concentration at the interface. From this the thickness of a boundary layer (z) can be estimated which is assumed to be in equilibrium with the organic phase in the pool in analogon to the transport of VOC across the capillary fringe (I.4). For more details see Eberhard and Grathwohl, 2002.

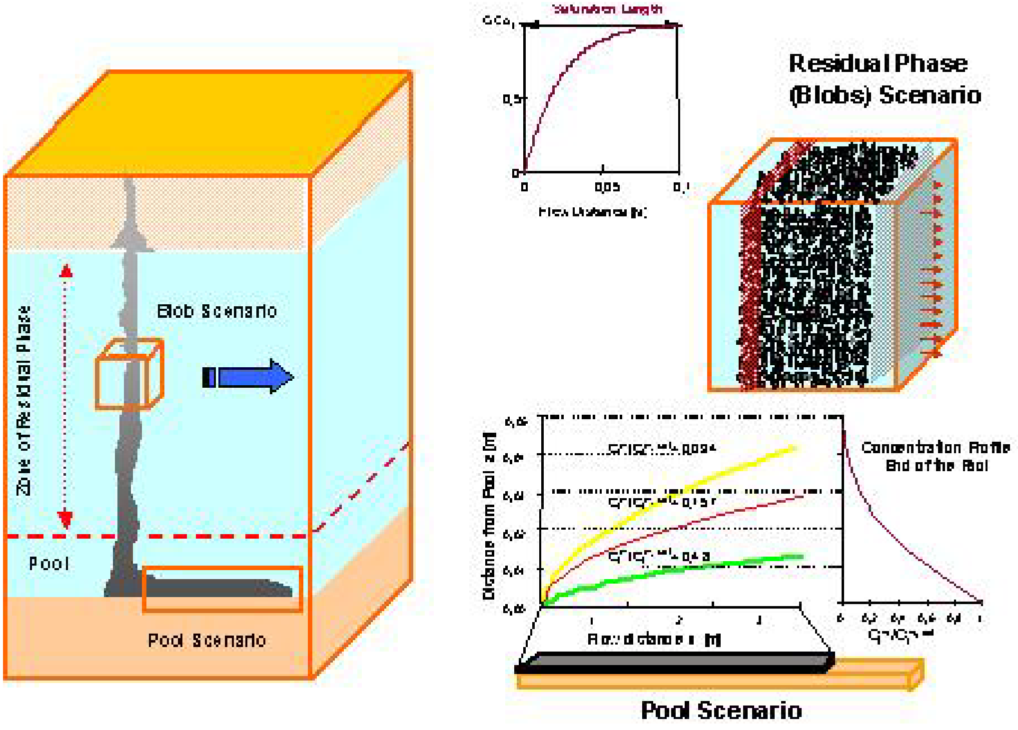


Figure II.4.1: *Conceptual model of the two contamination type scenarios (pool scenario/blob scenario).*

II.4.5 Concentrations and time scales for NAPL dissolution

Blob Dissolution

The minimum time scale of dissolution of the phase constituents from the blob zone can be estimated in a first approximation from the retardation of the dissolution front for the individual compounds. The time necessary to remove individual compounds differs with the physical-chemical characteristics (e.g. BTEX compounds from the 0.5 m long blob zone is from weeks to years and up to decades for the PAHs).

Pool Dissolution

Dissolution of coal tar pools show much longer time scales because of the small surface to volume ratio and the small values of the transverse vertical dispersivity. Time scales of dissolution of the mono-aromatic compounds are from decades to hundreds of years, while the release rates of the PAHs are predicted to be stable over several hundreds to thousands of years. In these estimates biodegradation is not considered. High biodegradation rates close to the pool/water interface could result in a steeper concentration gradient leading to a proportional increase of dissolution rates.

Lessons learnt and recommendations

Contaminated release from complex organic mixtures: Prediction of ageing behaviour

✓ Although most **compounds in complex organic mixtures** such as coal tar, creosote, and fuels are biodegradable, such **contaminant sources are very persistent over many decades to centuries** after the contamination occurred due to slow dissolution kinetics.

✓ Generally **two contamination scenarios types** can be distinguished:
  1) **Pools of organic phases**, e.g. if an DNAPL phase encounters low permeability domains in the subsurface and
  2) **Residual NAPL saturation** (e.g. > 3 % - 5 %) trapped in an aquifer as NAPL-blobs and ganglia.

✓ At sufficiently high residual NAPL saturation (e.g. > 3 % - 5 %) the **dissolution of NAPL-blobs** and ganglia takes place under equilibrium conditions even within short flow distances along the flow direction.

✓ The **minimum time for removal of a NAPL constituent from a "blob-zone"** can be estimated from the velocity of the dissolution front of compound *i*, which is retarded compared to the groundwater (retardation increases with the fraction of entrapped NAPL and decreases with increasing solubility of the compound; for solid compounds the sub-cooled liquid solid has to be used).

✓ ***Dissolution of* coal tar *pools*** show much longer time scales because of the small surface to volume ratio and the small values of the transverse vertical dispersivity. Time scales of dissolution of the mono-aromatic compounds are from decades to hundreds of years, while the release rates of the PAHs are predicted to be stable over several hundreds to thousands of years.

II.5 Diffusion limited desorption and modelling

Lead Authors: Hans van der Sloot, Rob Comans, Rainer Henzler, Peter Grathwohl

II.5.1 Simple first order approximation

Release modelling to describe a source term can be done relatively simple by using a CSTR (continuous stirred tank reactor) model description. Depending on the problem to be dealt with a more sophisticated approach using dual porosity and combined chemical reaction transport can be necessary. The simple CSTR model results in a exponential decrease of concentration with time.

In Fig. II.5.1 the results of this modelling approach is illustrated for sulfate leaching from MSWI bottom ash. For contaminants that are largely controlled by solubility constraints or by (de)sorption reactions, the quality of the predictions at long term are often acceptable in view of other uncertainties in the whole process, such as sample heterogeneities, attenuation and preferential flow issues. For contaminants with very limited matrix interaction, the uncertainty is largely caused by preferential flow aspects. At high L/S, which automatically is linked to a long time scale uncertainties of a factor of 2 are quite acceptable.

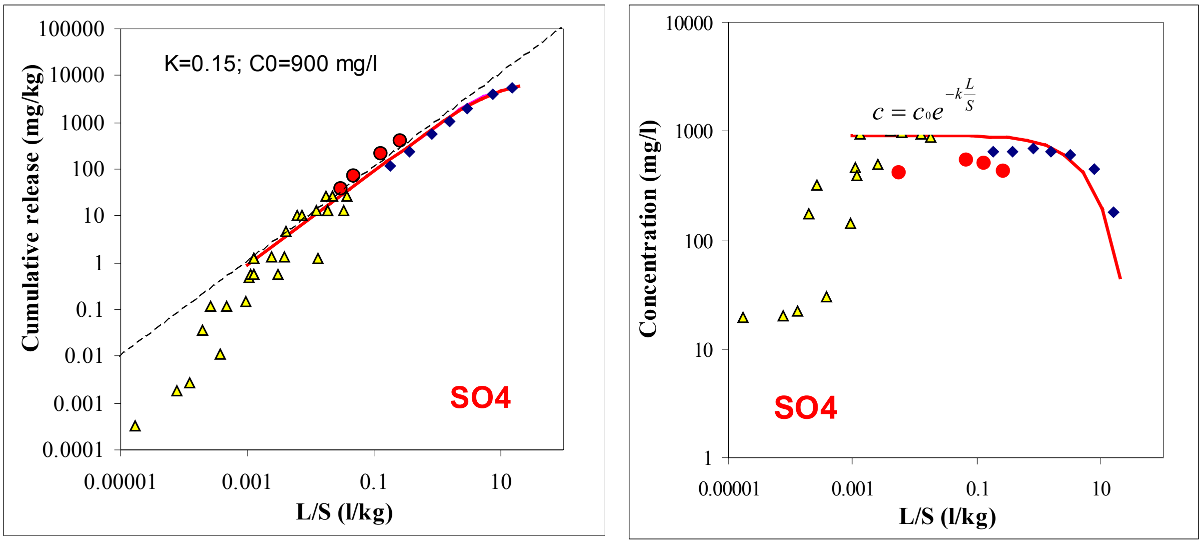


Figure II.5.1: *CSTR modelling of release from laboratory, lysimeter and field data from a predominantly inorganic landfill. Left graph: cumulative release; right graph: concentration as function of L/S.*

II.5.2 Diffusion limited release

In many cases, organic contaminants are sorbed on materials, especially on organic matter inside granular materials. In this case the contaminant release is diffusion limited. If the contact time between the percolating water and the contaminated material is not long enough to reach equilibrium conditions, the concentration in the leachate decreases over time from the beginning of the test (e.g. column percolation). For coarser materials and smaller intraparticle porosities it is more probable that the contaminant release takes place under non-equilibrium conditions. PAHs have different physical-chemical properties which affect the desorption behaviour. With decreasing solubilities, the equilibrium distribution coefficient K_d increases. The higher K_d the higher is the probability that the release takes place under equilibrium conditions and a longer equilibrium release time occurs, respectively.

Example: Fig. II.5.2 shows the results of a column leaching test (according to DIN V 19736) with demolition waste (symbols). The simulations were done with the numerical model SMART (solid lines), which was developed at the Universitiy of Tübingen (see Appendix 5). The model is based on the intraparticle diffusion from spherical grains with different sizes. At the beginning, all four chosen PAHs show equilibrium conditions and as expected in the sequence for Naphthalene (Nap), Acenaphtene Ace), Phenanthrene (Phe) and Fluoranthene (Fth) non-equilibrium conditions develop after differing periods of time.

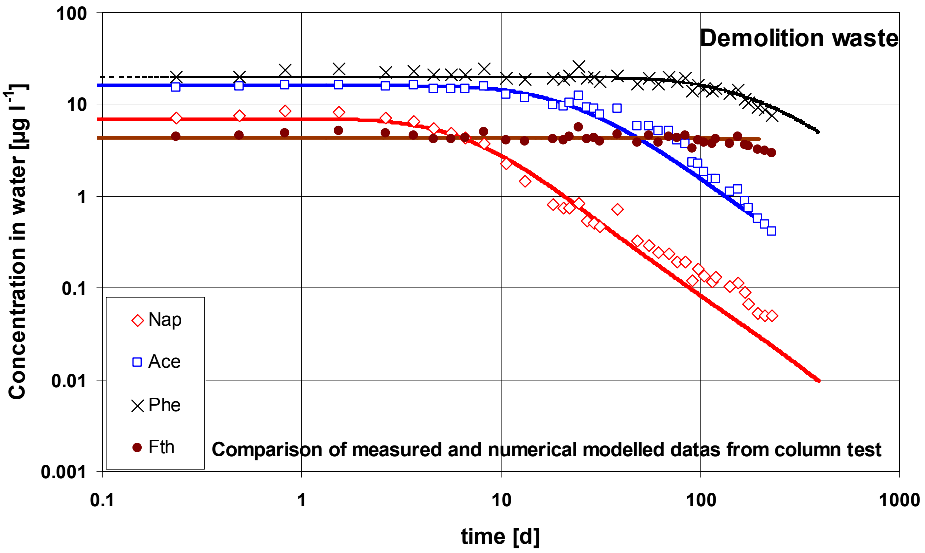


Figure II.5.2: *Measured data from a column test (symbols) and predicted concentration using the numerical model SMART (solid lines). For simulations with SMART, the following input parameters were used:* Material parameters: *Intraparticle porosity ε: 1,5 %, empiric coefficient* m *(to account for the tortuosity): 2 [-]; seven grain size classes between 0,02 mm and 4 mm.* Column parameters: *Diameter 6 cm, height 15 cm, porosity* n *0,27 [-] and velocity 1 m* d^{-1}. Chemical parameters: *Aquatic diffusion coefficient* D_{aq} *[*cm^2 s^{-1}*] from literature, the concentration in the solid phase are: Naphthalene =0.116 [mg* kg^{-1}*], Acenaphthene=0.886 [mg* kg^{-1}*], Phenanthrene=9,44 [mg* kg^{-1}*], Fluoranthene=10.0 [mg* kg^{-1}*]. The equilibrium distribution coefficient* K_d *was calculated with the determined equilibrium concentrations in water (for Naphthalene=15 [l* kg^{-1}*], Acenaphthene=60 [l* kg^{-1}*], Phenanthrene=473 [l* kg^{-1}*], Fluoranthene=2325 [l* kg^{-1}*]).*

Lessons learnt and recommendations

Diffusion limited desorption and modelling

- ✓ **Release modelling** to describe approximations of a source term can be done relatively simple by using a CSTR (continuous stirred tank reactor) model description. Depending on the problem to be dealt with, a more sophisticated approach using dual porosity and combined chemical reaction transport can be necessary.

- ✓ **Diffusion limited release** occurs when organic contaminants are sorbed inside porous particles.

- ✓ If the **contact time between the percolating water and the contaminated material** in a column test is not long enough to reach equilibrium conditions, the concentration in the leachate decreases over time.

- ✓ For **coarser materials** it is more probable that the contaminant release takes place under **non-equilibrium conditions**.

- ✓ **Diffusion models** allow an excellent fit of release rates determined in column test if sufficient data on material properties are available (Fig. II.5.2).

II.6 Leaching tests for the assessment of materials in laboratory tests

Lead Authors: Hans van der Sloot, Rob Comans

II.6.1 Integration of all aspects for a specific case

Many factors may play a role in the ultimately desired source term description for a given site and before an evaluation of impact to soil and groundwater can be made. The key aspect is to link the different aspects in such a manner that estimates can be made that as realistically as possible match with reality. ENV 12920 provides some guidance in this respect, as the parameters relevant to make a decision on a specific question must be identified and quantified.

- Key aspects in this context are:
- Nature of the contamination – inorganic, organic, specific source
- Major release controlling conditions as dictated by the soil under consideration (pH, EC, Eh, DOC) and changes and the magnitude of such change in these parameters at long term
- Leaching behaviour of the specific soil under consideration (possibly in relation to existing information on similar soils tested before)
- Information on hydrology in simple terms or more sophisticated
- Modelling to predict release as a function of time is a key aspect in this evaluation of a time dependent source term – uncertainties in the extrapolation are important to take along
- Verification data where possible from field observations
- Data presentation in forms such that comparison with regulation is meaningful and appropriate

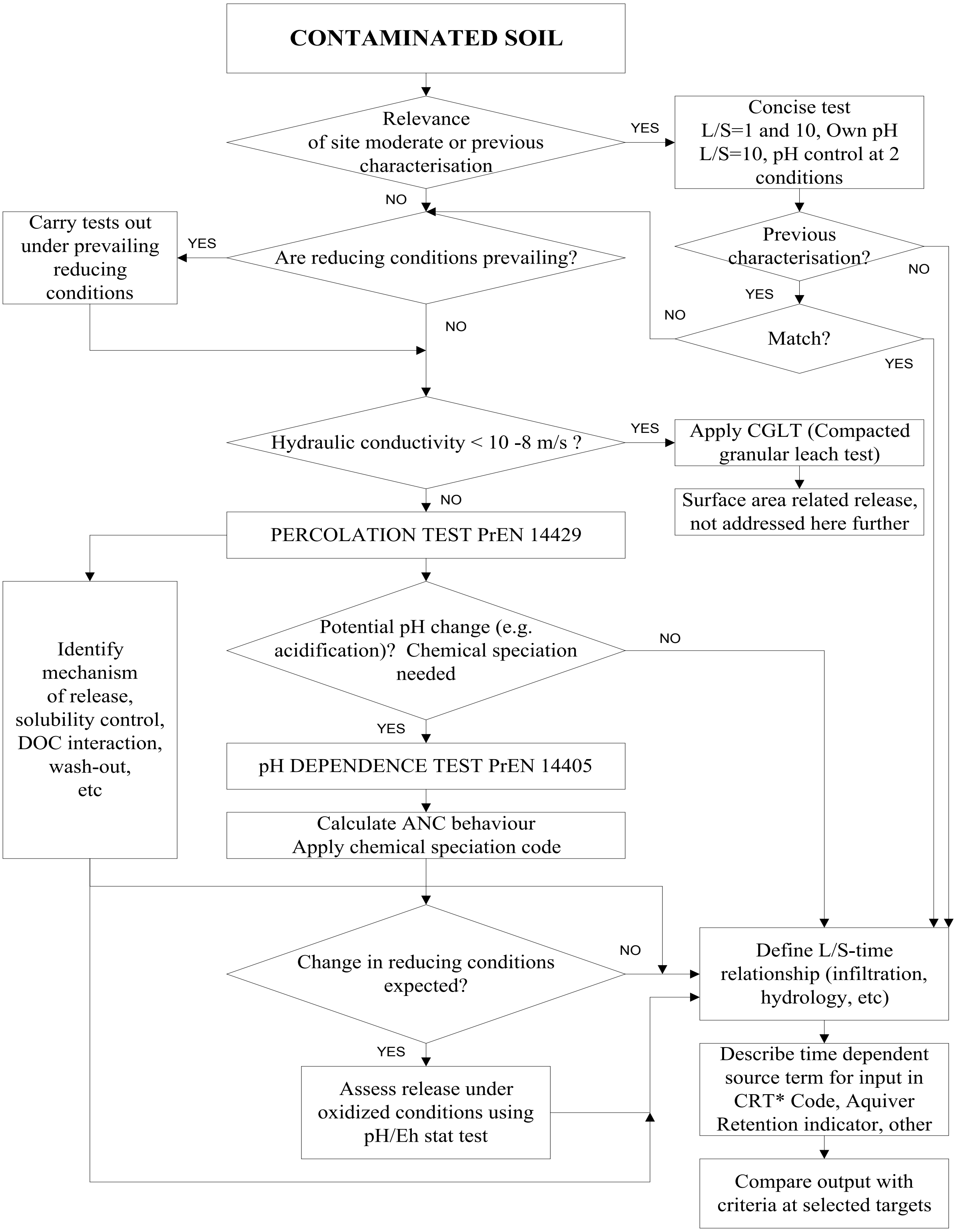
In Fig. II.6.1 a flow diagram illustrating decisions in test choice and conditions is presented.

The time dependent source term is derived from the percolation test data and modified as needed based on external factors, such as pH change with time and change in redox condition, using pH dependence leaching test data, ANC information in relation to external stresses and a quantification of release under other redox conditions. For a simple case, this information may come as a set of parameters describing the release as a function of time (CSTR or similar model) or in the form of a more sophisticated description.

Characterisation of soil and soil like material by means of more sophisticated test methods calls for a systematic electronic storage of such data in an easy retrievable manner. This is important as:

- reference for compliance and quality control test data
- basis for development of regulation and limit values
- means to limit unnecessary duplication of work
- means to focus on key parameters for specific materials
- to find consistency in test results between seemingly widely different source materials

A database /expert system is in development at ECN in co-operation with Vanderbilt University Nashville (USA) and DHI (Denmark). The database is in MS Access format and the expert system operates using Excel. More sophisticated codes (e.g. and geo-chemical modelling software (PHREEQC or ORCHESTRA) can be called from Excel to perform specific calculations using data retrieved from the database. Data from any type of leaching test, landfill leachate, data from lysimeter tests and pilot studies as well as groundwater data can be inserted and processed. The contaminants for which data are available in the database range from major, minor and trace elements, a large number of organic contaminants to radio-nuclides. Data have been collected from about 20 years of testing a wide range of different materials. Currently it contains about 660 samples with pH stat test and single batch test data, about 160 percolation test results, about 350 monolithic leaching test data and leachate data on some 50 landfills. This encompasses some 180,000 contaminant concentrations apart from descriptive information (further information can be obtained from www.leaching.net) In ENV 12920 (Methodology guideline) the outline and justification of choices that need to be made to reach an answer on a given problem definition. In a recent paper by Kosson et al (2002). The framework for evaluation and management of waste and construction materials is described, which has many elements that are needed for a proper judgement on acceptability. The ECN database/expert system is based on the concepts described in both documents.



* CRT - Chemical reaction / transport Code (e.g. Modflow)

Figure II.6.1: *Flow diagram of decisions depending on the conditions encountered.*

In the flow scheme given in Fig. II.6.1 the different aspects of describing a source term and impact on soil and groundwater for a contaminated site is given. Tab. II.6.1 gives examples of materials for which extended leaching information is already available.

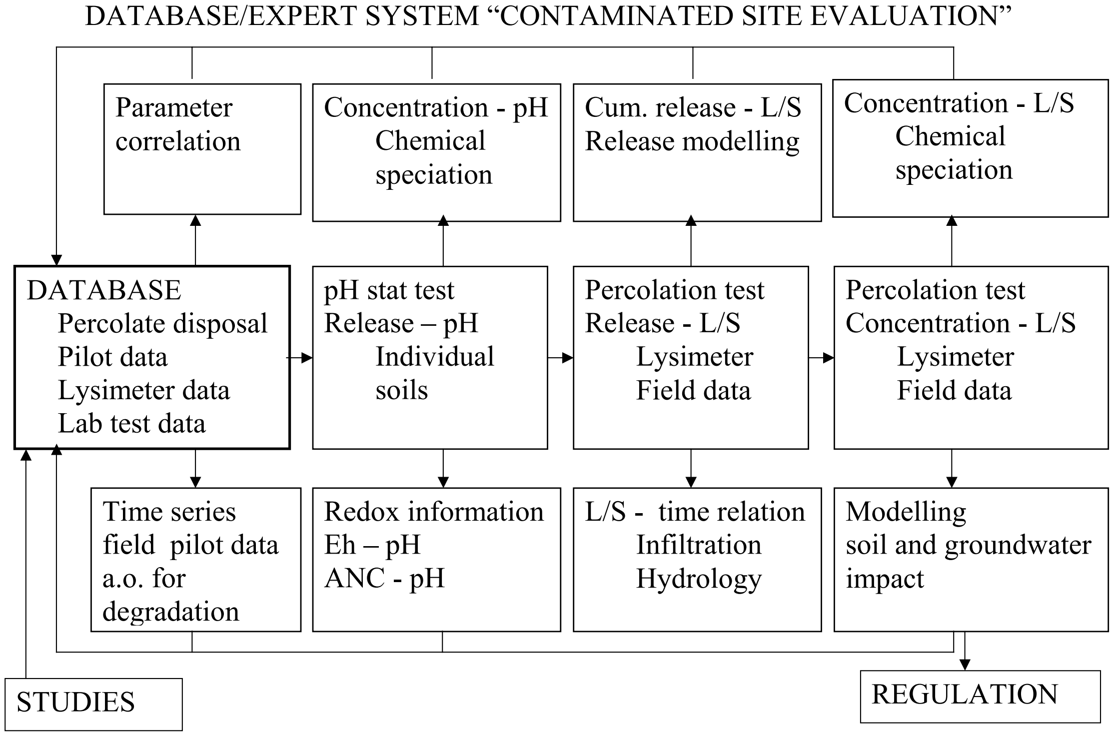


Figure II.6.2. *Flow scheme for the database/expert system to assess the source term and environmental impact of a contaminated site on soil and groundwater.*

II.6.2 Database/expert system

The database/expert system takes changes with time into account and integrates testing at different levels (lab, lysimeter, field) as well as external factors (pH, redox, complexants) and modelling (long-term) release as a function of these parameters. Hydrology is another aspect that links laboratory testing to the field situation. Impact to soil and groundwater can be modelled with relatively simple models or when needed with rather sophisticated ones. So besides a hierarchy in leaching tests methods, there is also a hierarchy in modelling. This means that complexity is applied and available when needed, while more simple straightforward verification is available for daily practice (see also speciation and impact modelling in section II.3.3). A unique aspect of the database is that the test data, lysimeter test results and field data are stored in a unified format, which allows mutual comparison of such widely different data. The format is also useful for mutual comparison of any leaching test. By combining such laboratory and field data with physical properties and hydrological aspects, scenarios can be build for almost any application and any material. This implies that a large number of different questions can potentially be answered.

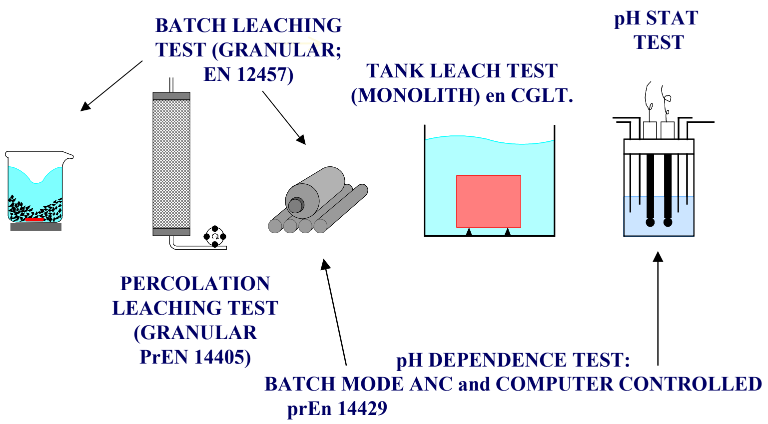


Figure II.6.3: *Relevant leaching test methods for granular and monolithic materials.*

Table II.6.1: *Materials for soil, soil related materials and materials with which soils may be contaminated, for which more extended leaching information is available (major, minor and trace elements as well as most relevant organic contaminants such as PAH, BTEX, mineral oil.*

Asphalt	Lava stone
Asphalt rubble	Lime stone
Basalt	Light weight concrete
Blast furnace slag	Lime silicate bricks
Bottom ash (coal)	Metalugical slag
Brown coal ash	Milling residues
Bricks (ceramic)	Mine stone (coal)
Clay bricks	MSWI bottom ash
Coal fly ash	PAH, PCB and metal polluted soil
Compost	Pb/Zn slag
Construction debris	Phosphate slag
Contaminated soil	Plastic waste material
Dredging sludge	Preserved wood
Dust form a sand blasting unit	Sand blasting waste
Steel slag	Sediments (river, lake, canal)
Tiles (ceramic)	Sewage sludge
Foundry sand (waste material)	Shredder waste
Glass-oven rubble formglass production	Sieve sand from demolition breaker
Soil amended with sewage sludge	Soil (various types of natural soil: sand, loam, clay)

Lessons learnt and recommendations

Leaching tests for the assessment of materials in laboratory tests

- ✓ The **short term data** obtained **from a laboratory leaching tests**, such as the percolation test can be modified to take relevant exposure conditions into account (pH, redox, etc).
- ✓ A **dedicated source term description** can be obtained by integrating lab, lysimeter and field data.
- ✓ A **decision scheme is provided**, which allows a **stepwise choice of tests and relevant conditions** needed to describe such a dedicated source term for the contaminants of interest.

II.7 Field validation of laboratory leaching procedure

Lead Authors: Hans van der Sloot, Rob Comans

As indicated in section II.2.1 under subheading “Relation between liquid/solid ratio (L/S) and time; testing at different scale” the relevance of testing at different scales was mentioned. Laboratory tests have their limitations, which is related to the scale and the level of control over factors that influence leachability. A form of field validation is therefore the comparison of laboratory leaching test data with lysimeter leachate measurements and field or pilot scale test results for the same material. Testing has been carried out at three levels – laboratory testing (0.0005 m^3), lysimeter (1.5 m^3) and pilot scale (12,000 m^3). Uniform data presentation of results from these different scales of testing is crucial. As basis for data comparison the cumulative release as a function of L/S is used. In a landfill site taking largely inorganic wastes, which encompasses for a large part soil and soil related materials (soil clean-up residues, contaminated soil, contaminated sediment and some small industrial waste input), such comparison has been made by filling a pilot cell with selected wastes and by collecting sub-samples from all charges delivered to constitute a composite sample representative of the entire cell to fill a lysimeter and to fill a laboratory column to carry out PrEN 14405. The results of the eluate analysis data and the leachate collected from lysimeter and pilot cell are recalculated to allow presentation as cumulative release as function of L/S and concentration as a function of L/S. In Fig. II.7.1 data of this comparison are given for Pb, Mo and Cl.

The consistency of the data from very different scales is striking for constituents that are controlled by solubility, such as Pb and Mo. The laboratory data provide adequate prediction of long term leaching behaviour. For Cl, the behaviour is consistent, but the level of release differs between laboratory and field. For Na, K and Cl a factor of about 4 lower release in the field versus the lab is observed, which is attributed to preferential flow (van der Sloot et al, 2003b).

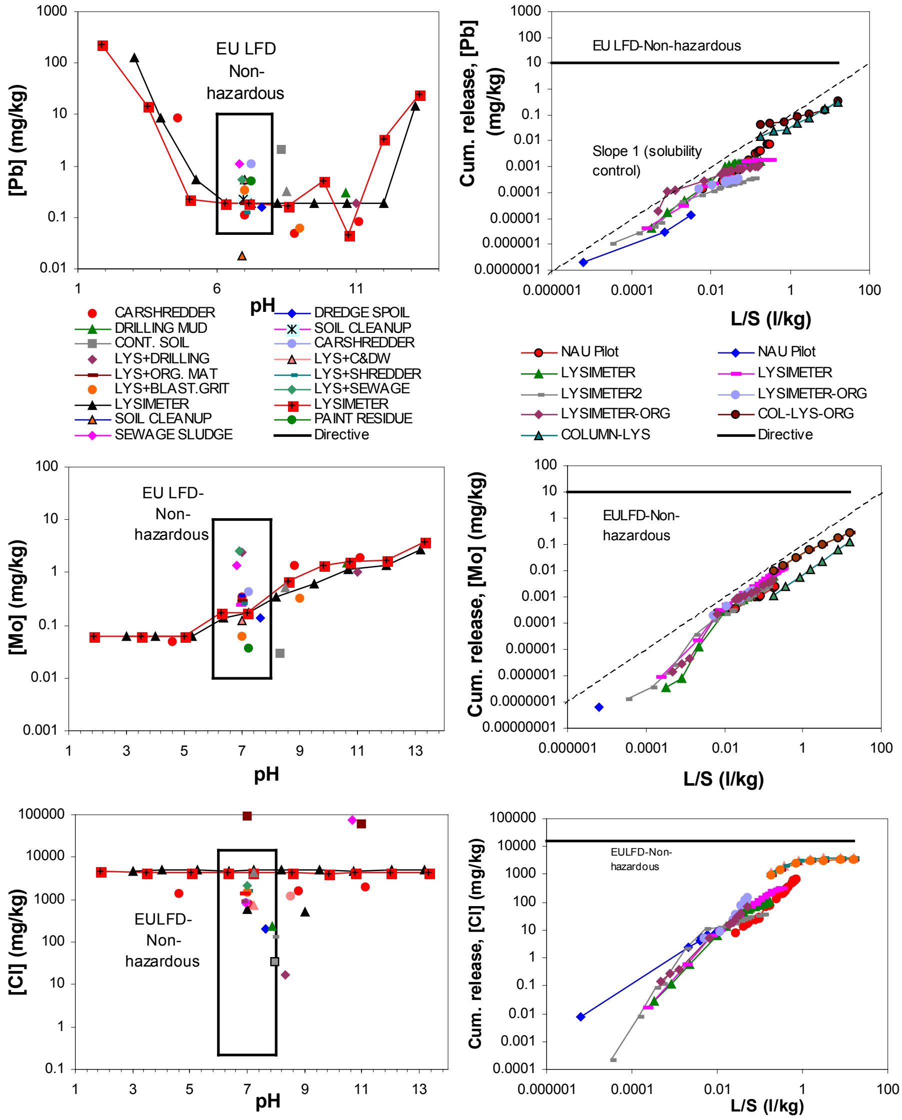


Figure II.7.1: Relationships between pH dependence and percolation test (laboratory) for Pb , Mo and Cl in a mixture of soil like wastes (integral mix) disposed in a 12,000 m^3 pilot cell with leachate data from individual wastes and from 1.5 m^3 lysimeters and the full scale pilot (see legend for specification of materials and tests).

Geo-chemical speciation modelling can confirm solubility control, for which an indication is obtained from column leaching tests by the slope 1 in the cumulative release –L/S plot. Using the new modelling environment ORCHESTRA (Meeussen, 2003) for geo-chemical solubility calculations with an extended MINTEQA2 database coupled to the Access database/expert system, the results of laboratory test data, lysimeter data and field leachate data can be evaluated simultaneously. Although the speciation has been calculated for many major, minor and trace elements, here the modelling results for Pb and Mo are given (Fig. II.7.2).

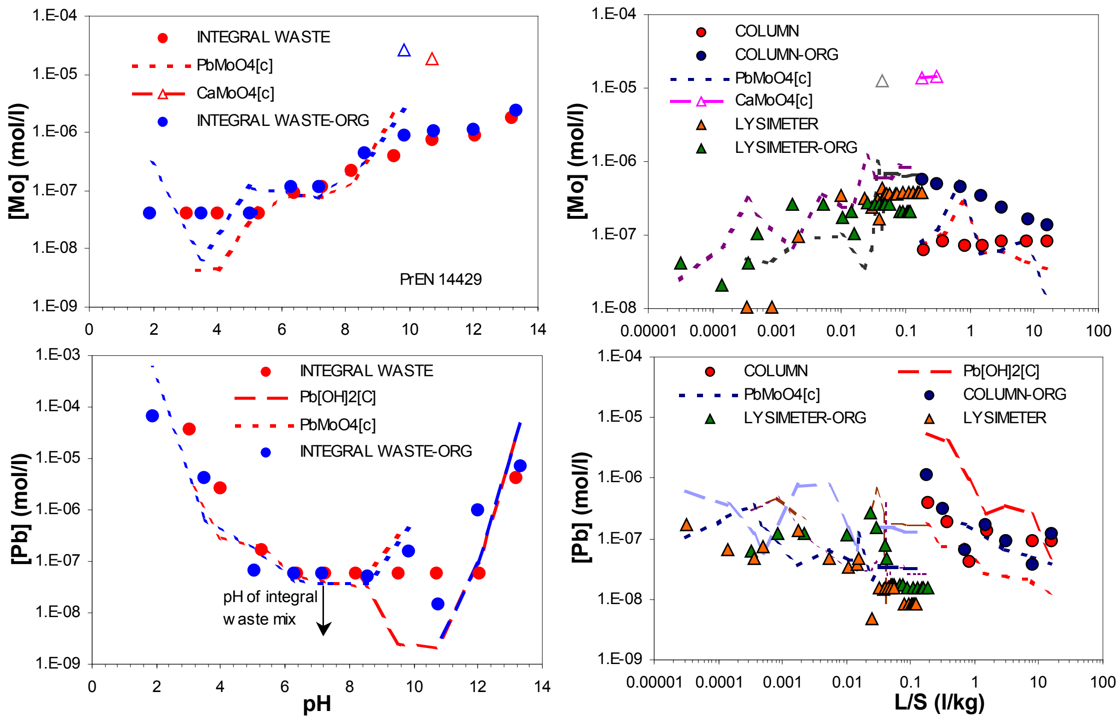


Figure II.7.2 *Geo-chemical modelling results for lead and molybdate for the different waste mixes tested in laboratory experiments and lysimeters.*

PbMoO4 seems to control solubility over a wide pH range (pH 2-8) and a very wide L/S range (0.0001 to 10). At pH above 10, the mineral Pb(OH)2 is relevant as it fits the pH dependence test data well. Above pH 10 no other relevant phases are identified for Mo as the solution is undersaturated with respect to CaMoO4.

The capability of calculating the chemical speciation of eluate data generated by the pH dependence test (pH variation), a percolation test (L/S variation) and leachate data (lysimeter and field) simultaneously, offers the possibility to draw conclusions on a large number of practical situations and time scales.

Lessons learnt and recommendations

Leaching of specific materials and phase modelling

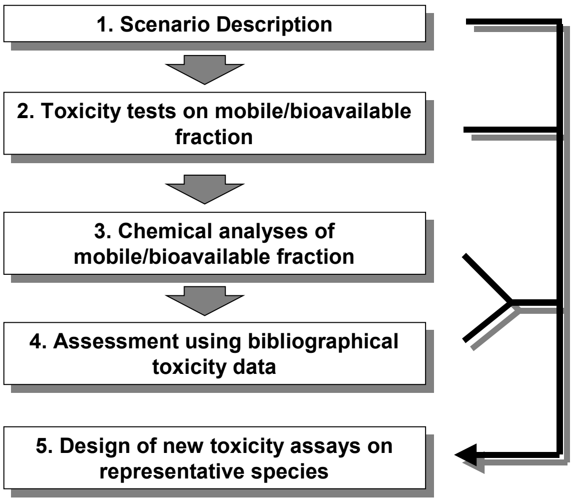
- ✓ The **consistent relationship** observed between laboratory, lysimeter and pilot (field) scale testing of the same complex mixture of materials holds **promise for the possibility to make predictions** of long term leaching behaviour.
- ✓ **Highly water soluble constituents** (irrelevant from a regulatory perspective) provide a means to **quantify the contribution** caused by preferential flow.
- ✓ **Geo-chemical modelling** of eluates and leachates resulting from complex mixtures is **possible** and can support/provide a **prediction of long term behaviour** and possibly future means to control release.

II.8 Toxicity Tests

Lead Authors: Alberto Bonilla, Iñaki Gorostiza

II.8.1 Introduction

Chemical analyses in conjunction with leachate and speciation tests provide information about the presence and concentration of contaminants as well as the mobility of these contaminants. However, they are not able to predict the harmful biological or ecological effects. Bioassays provide direct evidence of ecological effects associated with groundwater pollution, complementing conventional chemical analysis. Conventional biological tests applied in contaminated soil/waste assessment are based on the exposition of organisms to the pollutants and contaminated media of interest. These tests are performed in solid phase being expensive, and space and time consuming. This approach considers the use of bioassays traditionally applied in water monitoring or leachate ecotoxicity assessment. It is cheaper and has a quick response. This approach requires the development of extraction procedures. They should be used in conjunction with bio-assays in order to determine the hazards due to soluble molecules, less soluble molecules, soil bound molecules, etc. The combined application of extraction-leaching tests/bioassays/physico-chemical analyses on samples will provide complete information about the presence, behaviour and toxicity of pollutants in the tested materials. The next paragraph describes the step-wise approach developed for risk assessment involving leaching/toxicity tests.



For each scenario, several risk assessment steps of growing complexity can be considered. The more complex the assessment step, the higher are the costs and the time consumed. In addition, the significance of results can vary very much. From this point of view, groundwater environmental impact assessment involves several levels or steps that include procedures of increasing cost and difficulty. In the following paragraphs these steps are established and described with regard to the experiences gained during the GRACOS project.

II.8.2 Scenario description

A precise description of the contaminated site under study must be defined in order to carry out a fine-tuned ecotoxicological assessment of the impact on groundwater and contaminated leachates. Some of the most important points are:

- Type and features of contaminants
- Contaminants mobilisation mechanisms
- Hydrogeological, geological and other aspects related to existing mobilisation pathways
- Potential receptors of contaminants: Human beings / Aquatic ecosystems (Freshwaters/ Marine environments) / Terrestrial ecosystems

The objective for a scenario description will be the definition of the relevant contaminants (the mobile, available and/or toxic, ... contaminants), the potential migration pathways, the potential receptors of the contamination (human beings, aquatic organisms, terrestrial organisms, plants, etc.) and the potential exposure pathways. This process will rule the subsequent planning for the scenario risk assessment.

II.8.3 Fast/low cost toxicity tests on mobile/bioavailable fraction

The combination of leaching/mobility/bio-availability procedures and toxicity tests configure a simple and fast procedure for the assessment of ecological impact of contaminated materials. As toxicity tests are not specific for chemicals they can be used as a general indicator for environmental impact assessment of contamination. This approach can avoid the expensive and complex multi-parametrical analytical work.

Fast/low cost toxicity tests include different bioassays, such as Microtox and Lumistox, Toxkits, Chromotest, MetPlate, MetPad, etc. The appendix A6 (“procedures”) gives a brief description of some of these methods. In the framework of the GRACOS project Microtox and MetPlate bioassays have been carried out. Concerning these methods, the combination of extraction tests with Microtox bioassays on obtained mobile/bioavailable fractions have offered very good results.

Concerning toxicity bioassays and assessment, Microtox represents one of the tests most widely applied. Therefore, the application of this method is recommended if possible. The toxicity bioassays provide the EC_{50} value. This parameter represents the concentration of "toxic substances" that affects 50% of a group of exposed organisms. In some cases a linear correlation does not exist between chemicals concentrations and EC_{50} values. This is because of the possibility of synergic effects between contaminants or the possibility of existence of toxic components not analysed. But generally, good relation can be found between chemical and ecotoxicological data. Thus the EC_{50} can be employed as a valuable indicator of the contamination in groundwater. In the framework of the GRACOS project, a good correlation has been achieved between results from chemical characterisation of leachates (concentration of contaminants) and toxicity assays (EC50) as well.

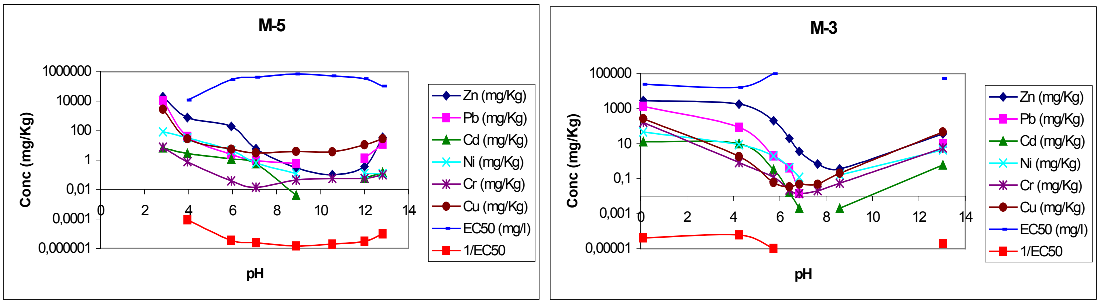


Figure II.8.1. *Release of heavy metals of a waste (M-5) and a sediment (M-3) and toxicity response of leachates (EC50) for pH-stat leaching tests.*

An essential point in the selection of the extraction agent is the fact that it must not introduce toxicity, otherwise the toxic behaviour of contaminants will be "masked". Therefore a blank test with the extractant must be carried out before its use. The results obtained from the combination of extraction procedures with low cost/fast toxicity tests (i.e. Microtox), can be used for a better planning of subsequent analytical determinations: sampling selection for instance. This procedure can optimise the economical effort for the assessment of a potentially contaminated site.

II.8.4 Ecotoxicological assessment based on the chemical characterisation of mobile/bioavailable fraction

In addition to the chemical characterisation of groundwater, different extraction procedures have been developed in order to get to know the mobility of contaminants from several matrixes and under several conditions to know the potential release of contamination to the groundwater. These extraction procedures allow the determination of bioavailable fractions from soils, sediments and other potentially contaminated media as well (see appendix A6 "Procedures"and section II.5). For ecotoxicological purpose the mobile/bioavailable fraction is considered as the most important fraction in the assessment of environmental/ecological risks.

For ecotoxicological assessment both data – groundwater and mobile fraction concentrations – can be compared with bibliographic toxicity values for the evaluation of groundwater ecological effects. An identification of potentially affected organisms must be carried out. There are several toxicity databases that include toxicity values for a wide range of organisms. The appendix A3 "Data from experiments and databases used" lists a set of public web pages involving possible databases to use for the performance of this assessment step. Toxicity data are updated very frequently.

Concerning groundwater eco-toxicological assessment, different organisms can be considered according to the involved media:

- Aquatic organisms (freshwater)
- Aquatic organisms (brackish or marine water)

Several calculations for the study of environmental impact on groundwater can be used (e.g. the model derived by Van Straalen and Denneman (1989)).

In conclusion, contaminant concentrations of mobile/bioavailable fractions of materials can be employed as a good reference tool for the study of potential hazards related to contaminated materials. However, these tests do not have in consideration contaminant synergetic effects. For this reason it is important to combine at this step chemical characterisation data with toxicity tests on groundwater/leachates that consider these synergetic effects and additionally take in consideration the effects of not analysed contaminants and other harmful factors. These reasons imply at certain situations a not direct relation between analytical and toxicological values. Using a conservative criterion the worst of both results can be used for risk assessment.

II.8.5 Toxicity tests on representative species of the evaluated scenario

Standard toxicity tests are based on a response in terms of mortality of primary organisms (usually bacteria) to a potentially contaminated medium (an aqueous contaminated medium in our case). The last step, which is the most accurate but the most expensive, could be the development of specific bioassays using representative species of the ecosystem sensible to the groundwater or to the mobile/bioavailable fractions. Obtained information from the previous step could be used for the planning of more valuable bioassays (i.e. selection of sensible species in the scenario or specifically sensitive to the detected contaminants) in order to economise available resources for the assessment. In the framework of the GRACOS project, comparison of mobile fraction toxicity of contaminated materials and bioassays on representative species of the studied scenario has shown a good relation between both responses.

Table II.8.2. *Comparison of leachates toxicity and bioassays (on a bivalve) results of a benthic scenario. Bioassays on Scrobicularia plana consist of exposure of the organisms to the contaminated media. The Toxicological effects will be related to the bioavailable fraction content of contaminants. This fraction is similar to that obtained from the batch leaching tests and good relation between both results has been achieved (N.E.: No Effect)*

	SD- 1	SD- 2	SD- 3	SD- 4	SD- 5	SD- 6	SD- 7	SD- 8	SD- 9	SD- 10	SD- 11	SD- 12
Batch Leaching tests	101,60	N.E.	410,60	399,30	311,60	N.E.	N.E.	250,70	N.E.	N.E.	N.E.	N.E.
***S. Plana* Average Survival**	8 ± 12	---	67 ± 12	79 ± 18	96 ± 6	92 ± 0	96 ± 6	---	100 ± 0	100 ± 0	100 ± 0	---

The development of toxicity tests focused on these specific organisms will provide a very valuable and site specific information about the ecotoxicological effects of contaminated groundwater. These assays must be carried out with more complex organisms (crustaceans, fishes, plants,…) than standard tests, and they are very expensive and space and time consuming. For this reason it is very important to define the existing situation as accurate as possible (developing previous steps) to plan the bioassays in order to have the maximum of information about ecotoxicological effects at minimum cost-effort.

Lessons learnt and recommendations

Toxicity Tests

- ✓ The **combined application of extraction-leaching tests/bioassays/physico-chemical analyses** on samples will provide a wide and complete information about the presence, behaviour and toxicity of pollutants in the tested materials.
- ✓ As **toxicity tests** are not specific for chemicals they can be used as a **general indicator** for environmental impact assessment of contamination. This approach can help in the planning and optimise the expensive and complex multi-parametrical analytical work.
- ✓ If necessary the results of the combination of extraction procedures with low cost/fast toxicity tests can be used for a **better planning of subsequent analytical determinations**.
- ✓ For **eco-toxicological assessment** both data – groundwater and mobile fraction concentrations – can be compared with bibliographic toxicity values for the evaluation of groundwater ecological effects.

Appendix

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A 1. List of symbols and abbreviations

1,2,4-TMB	1,2,4-trimethylbenzene
Ace	Acenaphthene
ANC	Acid neutralisation capacity
ATD	Automated thermal desorber
BA	Bottom ash
BTEX	Benzene, toluene, ethyl benzene, xylene
C_0	Initial concentration
C_g	Concentration in gas phase
CGLT	Compacted granular leaching test
C_{gn}	Normalised gaseous concentrations
C_{gr}	Concentration of contaminant in groundwater
$C_{i,avg}$	Depth averaged concentration of a compound
$C_{i,sat}$	Aqueous saturation concentration
C_i^{W}	Concentration of compound i in water
$C_i^{W,sat}$	Saturation concentration of compound i in water
CRT	Chemical reaction / transport code
CSTR	Continuous stirred tank reactor
C_W	Concentration in water phase
d	Density
D_{aq}	Aquatic diffusion coefficient
DNAPL	Dense non aqueous phase liquid
DOC	Dissolved organic matter
EC	Electric conductivity
EDTA	Ethylene Diamine Tetra Acetic acid
Eh	Redox potential
F	Flux
$f_{i,o}$	Fraction of the compound in organic mixture
Fth	Fluoranthene
GC	Gas chromatograph
H	Air-water equilibrium partitioning (Henry coefficient)
h	Height
Hac	Acetic acid
IR	Infra red
K	Release factor
K_d	Water-solid equilibrium distribution coefficient
$K_{sw}(x)$	Permeability horizontal
$K_{sw}(z)$	Permeability vertical
LNAPL	Light nonaqueous phase liquid
L/S	Liquid / solid ratio
L_p	Length of the pool
m	Empiric coefficient, to account for tortuosity
MIP	Membran interphase probe
MS	Mass spectrometry
MSWI	Municipal solid waste incinerator
N	Infiltration in mm/y
n	Porosity
n_e	Effective porosity
Nap	Naphthalene
NAPL	Non aqueous phase liquid
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyles
P_{gas}	Gas pressure
Phe	Phenanthrene
R_i	Retardation factor of compound i
S	Solubility
S°	Degree of NAPL saturation
SCE	Sequential Chemical Extraction
$\mathrm{s_m}$	Standard deviation of toxicity values

t	Time
TDR	Time Domain Reflectrometry
VOC	Volatile organic compounds
X	Length
x_m	Average of toxicity values
Z	Depth
z_a	Thickness of the aquifer
Z_S	Thickness of a boundary layer

Greek Symbols

α	Dispersivity
α_t	Transverse dispersivity
x	Length scale of contamination
$\chi_{i,o}$	Molar fraction
ε	Intraparticle porosity
$\gamma_{i,o}$	Activity coefficient
$v_{recharge}$	Groundwater recharge rate
θ	Volumetric water content
ρ_o	Density of the NAPL

A 2. References of the GRACOS project according to the main topics

Groundwater risk assessment at contaminated sites: General overview

Grathwohl, P., Klenk, I. (2000): Groundwater risk assessment at contaminated sites (GRACOS). In: W. Harder et al., (eds). ConSoil 2000, 831 - 834, Leipzig.

Grathwohl, P., Halm, D., Kjeldsen, P., Höhener, P. (2001): Groundwater Risk Assessment at Contaminated Sites. 1st Workshop SENSPOL: Sensing Technologies for Contaminated Sites and Groundwater, University of Alcalá (Madrid, Spain), 9 - 11 May, 2001, p. 123 – 133.

Grathwohl, P. and D. Halm (2001): Groundwater Risk assessment at Contaminated Sites (GRACOS). In: Seiler, K.-P., Wohnlich, S.: New Approaches Characterizing Groundwater Flow. Proceedings of the XXXI International Association Of Hydrogeologists Congress, Munich, Germany, 10-14 September 2001, Volume 1, 503-505.

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Characterisation of VOC contaminated sites

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A 3. Data from experiments and databases used

Biodegradation rates

Table A.1: *Biodegradation rates estimated at different experimental scales during the GRACOS project. Rates are given as apparent first order rates applied to the gaseous phase, in* d^{-1}*. See Refs. (1, 2) for definitions. For conversion to aqueous phase rates see equation 5 in ref. (1).*

	Alluvial Sand from Lake Geneva [a]				**Værløse Sand from 1 m depth [b] (GRACOS field site, Denmark)**	
Compound	**Column [c] Ref. (2)**	**Lysimeter [d] Ref. (1)**	**Batch tests [e] Ref. (2)**	**Column [f] Ref. (3)**	**Field[g] (MOFAT) Ref. (4)**	**Field[h] (MIN3D) Ref. (5)**
	d^{-1}	**d^{-1}**	**d^{-1}**	**d^{-1}**	**d^{-1}**	**d^{-1}**
n-Pentane	<0.01	<0.05	< det.limit	n.d.	n.d.	n.d.
n-Hexane	0.26	0.4	0.65±0.35	0.10±0.04	0.054	0.004
n-Octane	5.0	6.7±1.7	10.4±2.8	1.23±0.2	1.06	1.08
n-Decane	13.5	5	< det.limit	5.83±1.1	4.3	3.53
Cyclopentane	n.d.	n.d.	n.d.	0.04±0.04	n.d.	0.02
Cyclohexane	0.07	0.5±0.3	< det.limit	n.d.	n.d.	n.d.
Methyl-cyclopentane	0.1	0.15	< det.limit	0.12±0.08	n.d.	0.18
Methyl-cyclohexane	0.16	0.8±0.4	< det.limit	0.31±0.08	n.d.	0.10
3-Methyl-pentane	n.d.	n.d.	n.d.	0.06±0.02	n.d.	0.01
Isooctane[i]	0.09	0.12±0.03	< d.l.	0.20±0.01	0.15	0.01
Benzene	n.d.	n.d.	n.d.	0.21±0.12	0.63	1.95
Toluene	1.31	3.2	1.95±0.53	0.70±0.2	0.47	0.27
m-Xylene	3.28	n.d.	3.68±1.21	1.65±0.6	n.d.	1.65
1,2,4-Trimethyl-benzene	4.98	n.d.	< det.limit	3.70±0.4	n.d.	2.56
MTBE (Methyltert-butylether)	<0.01	<0.05	< det.limit	n.d.	n.d.	n.d.

[a] Nutrient-rich sand, with parameters described in Ref. (1) , [b] Glacial melt-water sand, low in nutrients, with parameters described in Ref (3) , [c] Soil water content θ_w=0.118, Temperature T= 23±2°C, [d] θ_w=0.05, T= 18±2°C, [e] θ_w=0.05-0.13, T= 25°C, batch data affected by non-steady state sorption (2), [f] θ_w=0.094, T= 25±2°C, [g] inverse modeling using model MOFAT, [h] inverse modeling using MIN3D, [i] 2,2,4-Trimethylpentane

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Physicochemical properties

Table A.2: *Physicochemical properties of compounds which were investigated in GRACOS*

	Compound	**Density [g mL^{-1}]**	**Molecular Weight [g mol^{-1}]**	**Boiling Point (^{0}C)**	**Vapour Pressure (pure compound) 25 ^{0}C [kPa]**	**Vap.Pres. (pure compound) temp. dep.**	***H*[-] 25^{0}C**	***H temp. dep.***	***Log K$_{ow}$***	***Water Solubility* [mg/l] 25°C**	**Water sol. temp. dep.**
Aromatic	Benzene	0.8765	78.11	80.1	12.672[5]	**For t = 5.0-50°C[5]** Log(p[kPa])=6.02994 -1211.033/(T[K]-52.36)	0.217[3]	**For t = 15.0-45°C** [3]: logK$_H$=a-b/T[^{o}K] a=7.15, b= 1397 logH=A-B/T, T[K][13] A = 5.053; B = 1693	2.13[1]	1790[6]	**Fort=5.0-50°C[5]** LogS=-15.544647 +1442.4276/T[K] + 3.2831x10^{-5} T^2
	Toluene	0.8667	92.14[2]	110.63	3.805[5]	**For t = 5.0-50°C[5]** Log(p[kPa])=6.02994 -1391.005/(T[K]-48.974)	0.244[3]	**For t = 15.0-45°C** [3]: logK$_H$=a-b/T[^{o}K] a=7.94, b= 1621 logH=A-B/T, T[K][13] A =5.271; B = 1745	2.73[1] 2.69[2]	556[5]	**Fort=5.0-50°C[5]** Log S=-46.05 +7268.85/T[K] + 1.411x10^{-4} T^2
	m-Xylene	0.864	106.17	139.1	1.106[5]	**For t = 5.0-50°C[5]** Log(p[kPa])=6.134008-1462.266/(T[K]-58.045)	0. 26[7]	logH=A-B/T, T[K][13] A = 6.532; B = 1491	3.20[1]	158[6]	Not found
	1,2,4 Trimethyl-benzene	0.8761	120.19	169.3	0.271[5]	**For t = 5.0-50°C[5]** Log(p[kPa])=6.16866 -1573.267/(T[K]-64.586	0.28[8]	logH=A-B/T, T[K][13] A = 6.532; B = 1491	3.78[1]	57[4]	**Fort=5.0-50°C[5]** LogS=-8.760–868.70/T[K]
n-Alkanes	Butane	0.579	58.13	-0.5	243.00[9]	**For t=-77-19°C[10]** Antoine eq.$^{\Delta}$: A = 6.80896 B = 935.86 C = 238.73	38.69[9]	Not found	2.89[14]	61.4[10]	Not found
	Pentane	0.626	72.15	36.1	68.40[9]	**For t=-50-58°C[10]** Antoine eq.$^{\Delta}$: A = 6.85296 B = 1064.84 C = 233.01	50.46[9]	Van'tHoff eq.*: ΔH$_{Henry}$6.1784 kJ/mol [12]	3.45[14]	38.5[14]	
	Hexane	0.660	86.17	69.0	20.20[9]	**For t =-25-92°C[10]** Antoine eq.$^{\Delta}$: A = 6.87601 B = 1171.17 C = 224.41	68.58[9]	Van'tHoff eq.*: ΔH$_{Henry}$ 6.1884[12]; ΔH$_{Henry}$= 65.793 kJ/mol[13] **For t = 10-30°C**[13] log H = A-B/T, T[K] A = 12.15; B = 3143	4.11[14]	9.5[14]	Not found

	Compound	**Density [g mL^{-1}]**	**Molecular Weight [g mol^{-1}]**	**Boiling Point (^{0}C)**	**Vapour Pressure (pure compound) 25 ^{0}C [kPa]**	**Vap.Pres. (pure compound) temp. dep.**	***H*[-] 25^{0}C**	***H temp. dep.***	***Log K$_{ow}$***	***Water Solubi-lity* [mg/l] 25°C**	**Water sol. temp. dep.**
	Heptane	0.684	100.21	98.4	6.11^{9}	**For t =-2-124°C^{10}** Antoine eq.$^{\Delta}$: A = 6.89677 B = 1264.90 C = 216.54	92.79^{9}	Van't Hoff eq.*: ΔH_{Henry}4.458 kJ/mol^{13} **For t = 26-45°C**^{13}: log H = A-B/T, T[K] A = 6.532; B = 1491	5.00^{14}	2.93^{14}	Not found
	Octane	0.703	114.23	126.0	1.88^{9}	**For t□-152°C^{10}** Antoine eq.$^{\Delta}$: A = 6.91868 B = 1351.99 C = 209.15	121.0^{9}	Van't Hoff eq.*: ΔH_{Henry} 6.1796^{12}; ΔH_{Henry}h.387 kJ/mol^{13} **For t = 26-45°C**^{13}: log H = A-B/T, T[K] A = 12.08; B = 3263	5.15^{14}	0.66^{14}	Not found
	Decane	0.730	148.28	174.1	0.175^{9}	**For tX-203°C^{10}** Antoine eq.$^{\Delta}$: A = 6.94365 B = 1495.17 C = 193.86	197.85^{11}	Van'tHoff eq.*: ΔH_{Henry}6.1676 kJ/mol ^{12}	6.25^{14}	0.052^{14}	Not found
	Dodecane	0.749	170.34	216.3	0.0157^{9}	**For t □-247°C^{10}** Antoine eq.$^{\Delta}$: A = 6.99795 B = 1639.27 C = 181.84	296.77^{11}	Van'tHoff eq.*: ΔH_{Henry}6.1671 kJ/mol ^{12}	7.24^{14}	0.0037^{14}	Not found
Cycloalkanes	Methylcyclo-pentane	0.7486	84.16	71.8	18.4^{2,15}	**Fort=-0.6-17.9°C**^{17}**:** P^{0} = 0.432 t +5.59 **Fort□.0-.6°C**^{15}: Antoine eq.$^{\Delta}$: A = 5.99178 B = 1188.320 C = 226.307	14.8^{15,18}	Van'tHoff eq.*: ΔH_{Henry}6.1730 kJ/mol^{12}	3.37^{1,20}	42^{21}	Not found
	Cyclopentane	0.7457	70.13	49.2	42.4^{16}	**Fort=-47.3-14.2°C**^{15}: Antoine eq.$^{\Delta}$: A = 6.25832 B = 1240.438 C = 242.957 **Fort□.7-50.0°C**^{15}: Antoine eq.$^{\Delta}$: A = 6.02877 B = 1133.199 C = 232.415	7.6^{4}	Van'tHoff eq.*: ΔH_{Henry}= 36.1835 kJ/mol^{12} **For t'.9-45.0°C**^{13}: log H = A-B/T, T[K] A = 5.162 B = 1302	3.00^{1,20}	156^{21,22}	Not found

	Compound	Density [g mL^{-1}]	Molecular Weight [g mol^{-1}]	Boiling Point (^{0}C)	Vapour Pressure (pure compound) 25 ^{0}C [kPa]	Vap.Pres. (pure compound) temp. dep.	*H*[-] 25^{0}C	*H temp. dep.*	*Log K$_{ow}$*	*Water Solubility* [mg/l] 25°C	Water sol. temp. dep.
	Methylcyclohexane	0.7694	98.19	100.9	6.13[16]	**Fort=-3.2-22°C[17]:** P^0 = 0.216 t +1.46 **Fort%.6-01°C[15]:** Antoine eq.$^\Delta$: A = 5.95366 B = 1273.962 C = 221.755	17.6[19]	Van'tHoff eq.*: ΔH_{Henry}= 36.2039 kJ/mol[12] **For t'.3-45.0°C[13]:** log H = A-B/T, T[K] A = 13.507 B = 3836	3.61[1,20]	14[21,22]	Not found
Isoalkanes	2,2,4-Trimethyl-pentane =Isooctane	0.692	114.2	99.2	6.56[14]	**For t=-79-25°C[24]:** $\log_{10}$(P[bar]) = A - (B / (T[K] + C)) A= 3.94736 B= 1282.332 C= -48.4	123.6[14]	Not found	4.09[28]	2.44[14]	Not found
	3-Methyl-pentane	0.664	84.16	64	25.3[14]	**For t□-63°C[25]:** $\log_{10}$(P[bar]) = A - (B / (T[K] + C)) A=3.97377 B= 1152.3 C= -46.021	68.6[14]	Not found	3.60[14]	12.8[14]	Not found
Freon	1,1,2-Trichloro-1,2,2-trifluoroethane ÏC-113	1.575	187.38	47.6	44.67[23]	P0 (25°C): 44.67 kPa[26] P0 (20°C): 36.31 kPa[26]	14.20[27]	Ref 27: Ln F = $a_1 + a_2(100/T) + a_3\ln(T/100) + a_4(T/100)^2$ F = Solubility in mol $l^{-1}atm^{-1}$ a1 = -230.016 a2= 320.338 a3= 118.173 a4= -1.3917 and H = 1/(RT F)	3.16[8]	170[29]	Not found

*Van't Hoff eq: ;ΔH[-] = Henry´s law constant at temperature T[K]; H_0[-] = Henry´s law constant at temperature T_0[K], ΔH_{Henry} = enthalpy of the reaction at standard conditions [J mol^{-1}]; R = universal gas constant (8.314 J mol^{-1} K^{-1}). $^\Delta$Antoine eq: log P^0 = A-B/(t+C), P^0 = vapour pressure (kPa for cycloalkanes and mmHg for alkanes), t = temperature (°C)

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A 4. Toxicity databases

- http://www.epa.gov/ecotox: The ECOTOX (ECOTOXicology) database provides single chemical toxicity information for aquatic and terrestrial life (terrestrial plants and terrestrial wildlife). Peer-reviewed literature is the primary source of information encoded in the database. Pertinent information on the species, chemical, test methods, and results presented by the author(s) are abstracted and entered into the database. It integrates three previously independent databases - AQUIRE, PHYTOTOX, and TERRETOX. The U.S. EPA Office of Pesticide Program's Pesticide Ecotoxicity Database (formerly Environmental Effects Database) of toxic effects data for registered pesticides is also included within ECOTOX. Not all data published in the peer review ecotoxicology literature are included in ECOTOX. In addition, it is recommended that you consult the original scientific paper to ensure an understanding of the context of the data retrieved from the ECOTOX database.
- http://risk.lsd.ornl.gov/homepage/eco_tool.shtml: As part of the RAIS (Risk Assessment Information System) web site, which contains Risk Assessment Tools and Information. The Risk Assessment Tools include: Risk-Based Preliminary Remediation Goal (PRG) calculations, a Toxicity database, Risk Calculations, and Ecological Benchmarks.
- http://data.pesticideinfo.org/PCW/Search_Ecotoxicity.jsp: The Pesticide Action Network Pesticide Database is a location for current toxicity and regulatory information for pesticides.
- http://toxnet.nlm.nih.gov/index.html: TOXNET is an integrated system of toxicology and environmental health databases that are available free of charge on the web. The following databases are available for searching via TOXNET: HSDB® (Hazardous Substances Data Bank), TOXLINE® (a bibliographic database), IRIS (Integrated Risk Information System), TRI (Toxic Chemical Release Inventory), CCRIS (Chemical Carcinogenesis Research Information System), GENE-TOX, DART®/ETIC (Developmental and Reproductive Toxicology/Environmental Teratology Information Center).
- http://www.geog.umn.edu/courses/5565/ceetvform20cfm.htm: For the Atlantic Coast region, the CEE-TV database contains approximately 4,000 records containing ecotoxicological exposure and effects information on over 150,000 individuals representing 200 species of amphibians, reptiles, birds, and mammals residing in estuaries. The database can be easily queried using taxonomic, chronologic, geographic and contaminant search categories.
- http://www.esd.ornl.gov/programs/ecorisk/ecorisk.html: This web site contains information that can be used to conduct ecological screening and baseline risk assessments. This site was prepared by the Environmental Sciences Division and Life Sciences Division of Oak Ridge National Laboratory for the U.S. Department of Energy. Partial support for this project was provided by the Strategic Environmental Research Development Program through DOE's Office of Environmental Policy and Assistance.
- http://www.rivm.nl/bibliotheek/rapporten: RIVM has published several documents that contain extensive literature review data on ecotoxicity of contaminants on terrestrial and aquatic species.

Effects on aquatic communities of the estuarine

Data from mobile fraction will be compared with Environmental Quality Guidelines (EQG) reference values for marine aquatic communities. EQG values correspond to those values for salty/marine water communities applied in Canada. In those cases where not salty/marine water values are available, freshwater reference value will be used.

Table A.5: *Comparison of mobile fraction concentration of contaminants with EQG reference values for marine aquatic organisms. White: Below EQG value and Black: above EQG value.*

	M1	M2	M3
As (ug/l)	5.5	4.95	60
Cd (ug/l)	12.4	4.25	1.95
Cr (ug/l)	6	5.05	6
Cu (ug/l)	51.5	49	4.95
Hg (ug/l)	< l.d.	< l.d.	< l.d.
Ni (ug/l)	72	36	61
Pb (ug/l)	< l.d.	< l.d.	5.2
Zn (ug/l)	640	515	2020

No significant concentration of organic compounds is found in mobile fraction from the column tests. On the contrary, most of the metal concentrations analysed in the mobile fractions of the batch leaching tests are above EQG reference value. Only As, Hg and Pb for samples M-1 and M-2, and Hg for sample M-3 appear below EQG reference level.

For a **more detailed assessment** of the ecological risk, the species sensitivity distribution method for the calculation of the theoretical potentially affected fraction (PAF) of species of the ecosystem will be applied. The method of Van Straalen and Denneman for the potentially affected sediment invertebrates will be applied. In order to calculate this number, a compilation of ecotoxicological data must be carried out and the concentration of the mobile fraction from the batch leaching tests will be used. Since not enough toxicity data was available for the calculation of the distribution curve of As, the most restrictive toxicity value will be employed for the comparison. As comparison is expressed as the ratio mobile fraction concentration: reference toxicity value, which means that values higher than 1 indicate concentration exceeding reference value.

Table A.6: *Theoretical potentially affected fraction (PAF) of species of the ecosystem.*

	M-1	M-2	M-3
As	---	---	0.095
Cd (%PAF)	0.00	0.00	0.00
Cr (%PAF)	17.79	17.46	17.79
Cu (%PAF)	0.00	0.00	0.00
Hg (%PAF)	---	---	---
Ni (%PAF)	23.81	23.19	23.66
Pb (%PAF)	---	---	1.70
Zn (%PAF)	40.93	40.66	42.35

No values higher than 10 % PAF has been detected for Cd, Cu, and Pb. Hence it can be considered that there is not a significant risk for the ecosystem due to the presence of these metals. PAF for Cr and Ni are around 20 %, which can be assumed as a moderate potentially risk. However, Zn reaches values above 40 %. This fact means an important level of risk for the ecosystem due to the presence of this metal. Concentration of As does not exceed the most restrictive toxicity value for this metal.

A 5. Numerical codes used

MOFAT (Katyal et al., 1991)

MOFAT is a two-dimensional (planar or radial) finite element program for multiphase flow and multicomponent transport in the subsurface. Three fluid phases – water, NAPL, and gas – are considered in the flow module. Up to five components can partition between these three phases with equilibrium or kinetically controlled mass transfer. Advection, dispersion and diffusion of all phases are taken into account in two dimensions. Sorption and degradation are possible in all phases. Relationships between phase permeability, saturation, and pressure are described by a three-phase extension of the van Genuchten model. MOFAT calculations of transport and attenuation extend in both vadose and saturated zones.

Katyal, A.K., Kaluarachchi, J.J., Parker, J.C., Cho, J.S., Swaby, L.G., (1991). MOFAT: A two-dimensional finite element program for multiphase flow and multicomponent transport, EPA/600/2-91/020.

R-UNSAT (Lahvis and Baehr, 1998)

R-UNSAT is a finite difference algorithm for ax symmetric, reactive, multispecies transport in the unsaturated zone. Gas diffusion and aqueous advection and dispersion are the main transport mechanisms, whereas sorption and biodegradation are the reaction mechanisms included. Calculations are performed in the gas phase. Biodegradation is studied in detail and consumption of oxygen with subsequent production of carbon dioxide can be included in the calculations. Monod kinetics is also a possible option. All of the processes are assumed to be in equilibrium. R-UNSAT can simulate the transport and fate of 7 components and offers the option of employing one-dimensional analytical solutions for simulating non-reactive, vertical transport in the unsaturated zone.

Lahvis, M.A., Baehr, A.L., (1998). Documentation of R-UNSAT, a computer model for the simulation of reactive, multispecies transport in the unsaturated zone, USGS.

MIN3P (Mayer et al., 2002)

The numerical model MIN3P (Mayer et al., 2002) was used for reproduction of the measured vapour phase plume and source evolution at Værløse field site in 3D. The code allows for the calculation of vapour phase transport, using the approach of Millington (1959), and unsaturated flow in the vadose zone (Richard's equation). The dissolution or degassing an organic compound mixture is simulated applying *Raoult's* law, equilibrium partitioning between aqueous and gas phase is implemented according to Henry's law. Biogeochemical reactions and transport processes are coupled by a global implicit solution method and solved using a finite volume algorithm. A variable number of geochemical compounds and reactions, such as biodegradation processes, can be handled based on an external database derived from the geochemical equilibrium model MINTEQ (Allison et al., 1991). Transient boundary conditions and time and depth dependent soil temperature profiles can be applied in the simulations. That way, data measured at the site could be directly implemented in the model. Unsaturated zone reactive transport modelling for the Værløse field experiment is described in detail in Maier et al. (2003, in preparation). The model was run accounting for 17 chemical compounds (13 kerosene constituents, the tracer freon CF113, and biodegradation reactants CO2, O2 and H+) and a 40 x 17 x 17 block grid. Grid size was constrained by the memory limitation of one Giga-Byte on a PC, resulting in a compromise between accuracy and computational capability. However, concentrations of compounds that are not sensitive to biodegradation like the non-degradable tracer CF113 could be reproduced well by the non-calibrated model already, simply applying compound, soil and weather characteristics determined at the field site. Biodegradation rate constants (pseudo first order with respect to the substrate concentration) were used as the only fitting parameter in the unsaturated zone. Due to long CPU run times of several days, simple eyeball fitting was applied comparing measured and simulated concentration time series at sampling ports below and one and two meters laterally from the kerosene source in a trial and error procedure. In total, about 15 runs were performed, with main focus on fitting the early 100 days (peak concentrations). Only simulations that fitted well in the beginning were continued. Biodegradation rate constants were obtained, by the best fit runs.

Mayer, K. U., Frind, E. O. & Blowes, D.W. (2002). Multicomponent reactive transport modeling invariably saturated porous media using a generalized formulation for kinetically controlled reactions. Water Resources Research 38(9): 1174-1195.

SMART *(Finkel & Liedl, 1997)*

The reactive transport model SMART (Streamtube Model for Advective and Reactive Transport) has been developed to describe transport of organic contaminants in heterogeneous porous media. The model is an adaptation of a Lagrangian method allowing for separate and efficient treatment of conservative transport and reactive processes. It accounts for the hydraulic as well as for the physico-chemical heterogeneity of porous media. In particular, the impact of preferential flowpaths on contaminant transport can be quantified. The reactive processes contained in SMART comprise: equilibrium and kinetic sorption / desorption of contaminants on the immobile subsurface material as well as on mobile particles, filtration of mobile particles and biodegradation of contaminants. The model is conceptualised as a pure forward model by addressing the physico-chemical heterogeneity of the subsurface material by means of a matrix of different grain size classes and lithological components, and by using independently measured parameters only.

Finkel, M. and Liedl, R.. Teutsch, G. (1999): Modelling Surfactant-Enhanced Remediation of Polycyclic Aromatic Hydrocarbons.- Environmental Modelling & Software 14: 203-211.

ECOSAT *(Keizer and Van Riemsdijk, 1996)*

ECOSAT (Equilibrium Calculation Of Speciation And Transport), is a computer program for the calculation of chemical speciation and mass transport in soil-water systems. Besides speciation (solution, mineral equilibria, sorption), ECOSAT can compute 1-dimensional and semi-2 dimensional stationary water or gas transport (multi component transport). Both speciation and transport calculations can include slow mass transfer (physical and chemical kinetics). The speciation core of this code is based on the well-known code MINEQL. The addition of sorption models, such as variable charge models (Basic Stern, Diffuse Layer, Constant Capacitance, Triple Layer) and non-variable charge models (Langmuir, Freundlich) has made the code useful for specific applications in the field of soil chemistry and soil pollution. The latest version (4.7) includes several recently developed mechanistic sorption models, such as the NICA-Donnan model for modelling sorption of contaminants to natural organic matter.

Keizer, M G and van Riemsdijk, W H. (1996). ECOSAT: Equilibrium Calculation Of Speciation And Transport, user manual, version 4.3. Wageningen, The Netherlands, Wageningen University and Research Centre (WUR); Subdepartment of Soil Quality (http://www.dow.wau.nl/soil_quality/).

NICA-Donnan model *(Kinniburgh et al., 1996)*

The NICA-Donnan model is part of a new generation of mechanistically based sorption models for modelling the complex interactions between metal cations and humic substances. In these models, the assumption is made that specific binding of protons and metals can take place at binding sites such as carboxylic and phenolic groups on the humic particle, which have an affinity for protons and metals that is not discrete but is distributed around certain peak values. Non-specific binding can take place in a diffuse layer around the humic particle particle, and is a function of surface charge and ionic strength. Recently, a very comprehensive "generic" set of parameters has become available for the NICA-Donnan model. The model is not a "stand alone" model code; there are currently only a few chemical speciation programs in which the model is incorporated, namely ECOSAT and ORCHESTRA.

Kinniburgh,D.G., Milne,C.J., Benedetti,M.F., Pinheiro,J.P., Filius,J., Koopal,L.K. & van Riemsdijk,W.H. (1996). Metal ion binding by humic acid: application of the NICA-Donnan model.Environmental Science and Technology, 30, 1687-1698.

ORCHESTRA *(Meeussen, 2003)*

ORCHESTRA (Objects Representing CHEmical Speciation and TRAnsport models) is a framework for implementing chemical speciation models, and for combining such models with kinetic or transport processes. The two main components of the ORCHESTRA framework are (1) a generic calculation kernel (Java executable) and (2) an object database (text file) with model definitions (calculation recipes). The object database contains objects that represent a number of basic chemical model elements such as "components", "species", "minerals" etc. which make it possible to use ORCHESTRA in a similar way to standard chemical speciation models such as MINTEQ, PHREEQC, or ECOSAT. Because the structure of the model definitions is object oriented and therefore very flexible, users can easily construct new models by defining model objects and keywords. A detailed description and examples can be viewed at http://www.meeussen.nl/orchestra/.

Meeussen, J.C.L. (2003). ORCHESTRA: An object-oriented framework for implementing chemical equilibrium models. Environmental Science and Technology, 37, 1175-1182.

A 6. Procedures

Leaching

The following leaching procedures are European (CEN) standards or European and international standards (ISO) in development:

Characterisation leaching tests

pH static leaching test

This test (PrEN 14429) provides information on the pH dependent leaching behaviour of the material. The test consists of a number of parallel extractions of a material at an L/S 10 during 48 hours at a series of pre-set pH values. Since pH is one of the main leaching controlling parameters, the information can be used to evaluate the repeatability in testing (resulting from measurement at steep concentration - pH slopes) and to provide information on the sensitivity to pH in specific field scenarios. The acid neutralization capacity (ANC) derived from the test is a useful property in this respect. For material characterization this has been proven to be a very useful method.

Column leaching test

In this leaching test (PrEN14405), 7 eluate fractions are collected within the range of L/S = 0.1-10 l/kg. The total duration is approximately 21 days. Leachant is demineralised water (DMW). The test material is applied as received (≈ 1 cm ∅) and upflow (14 ml/h) is applied through a column waste height of 28 cm and a diameter of 5 cm.

NEN 7345 Tank leach test

In this test the specimen is subjected to leaching in a closed tank. The leachant is renewed after 8 hours and 1, 2.25, 4, 9, 16, 36, 64 days at a leachant to product volume ratio (L/V) of approximately 5. The results are expressed in mg/m^2. This test is a procedure to evaluate the release from monolithic material by predominantly diffusion control (e.g. exposure of structures to external influences). The distinction is necessary, as the transport limitations set by a solid form result in a significantly lower environmental impact than derived from crushed material. This condition is valid as long as the product retains its integrity. To assess the behaviour after disintegration or demolition of monolithic forms, the information obtained in the pH dependence leaching test is very relevant, as in this situation the pH is likely to change to more neutral conditions.

Compacted granular leaching test NVN 7347 (Dutch pre-standard)

This test resembles the tank leach test for monolithic materials in the way it is carried out and the data are handled. The method is designed for granular materials that behave as a monolith in the scenario under investigation (e.g. clay lens in a sandy soil).

Compliance leaching tests

EN 12457. CEN/TC 292

Compliance test for granular materials EN 12457 - has been recently validated. Part 1 is an L/S=2 extraction on material < 4 mm. Part 2 is a single step extraction at L/S=10 using material < 4mm. Part 3 consists of two extraction steps at L/S=2 and subsequently at cumulative fraction L/S=10. Part 4 is an L/S=10 extraction on material < 10 mm. In the hierarchy of CEN/TC 292, this is a compliance test (level 2 test).

Compliance monolith leach test

Although still in development by CEN/TC 292/WG 2 the main test features are: the specimen is leached after vacuum saturation with demineralised water at an liquid to area ratio of 5, eluates are produced after 6, 24 and 48 hours and subsequently analysed.

The pH dependence test in combination with either a percolation or a dynamic monolith leach test will cover more than 80 % of the conditions that may be relevant to address questions of short and long term release for respectively granular - and monolithic materials. The compliance test are meant to be able to carry out a quick check if materials, that have been characterised sufficiently before with the characterisation leaching tests, show the same leaching behaviour and thus can be judged similarly as the previously characterised material.

Further leaching procedures

See: www.ecn.nl/library/horizontal (download hor_desk_23_leaching.pdf).

Manual for the setup of a column test (according to the German pre-standard DIN V 19736)

The column test is carried out to determine:

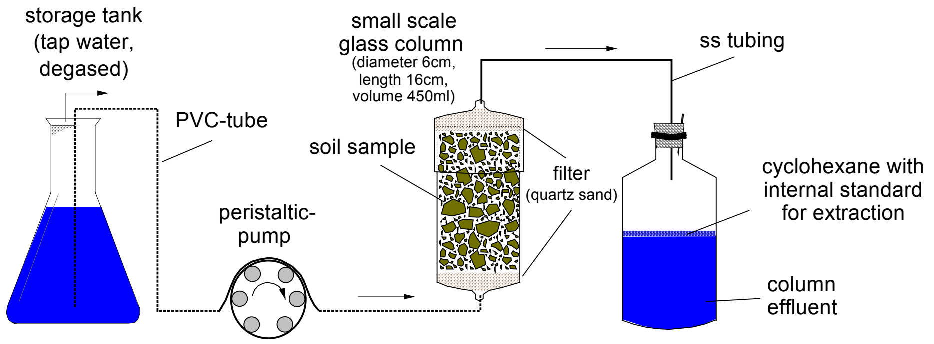
a) Concentrations of organic compounds in groundwater and

b) Leaching behaviour of different solid materials.

The description of the leaching test follows in essence the DIN V 19736 (October 1998). This leaching test is not suitable for silty and clayey soils with a hydraulic conductivity below a k_f-value of 10^{-6} m sec^{-1}. Silty and clayey soils can be leached in soil column tests, if the material exists in aggregated form or in small pieces.

Experimental setup

The water (degased drinking water) is pumped from the storage tank to the soil column with a peristaltic pump at a constant pumping rate (see Fig. A.1 – details see Fig. A.2). The soil column and the storage tank are connected by a PE-(PVC)pipe, whereas the column and the glass-collection-bottle are connected by a stainless steel pipe. The contaminated material is placed above a filter layer of quartz sand. This guarantees a steady inflow into the column. The soil column has to be percolated from the bottom to the top in order to prevent the trapping of air bubbles. The flow velocity in the column is adjusted to about 1m per day. The flow velocity of water in the soil column can be changed by the selection of different diameters of the pumping tubes and by the selection of different speed ranges of the peristaltic pump. Typical groundwater flow velocities in river aquifers of middle Europe are in the area of 1 m day^{-1}.



Column Leaching Test, Experimental Setup (schematic)

Figure A.1: *Schematic experimental setup for column leaching test.*

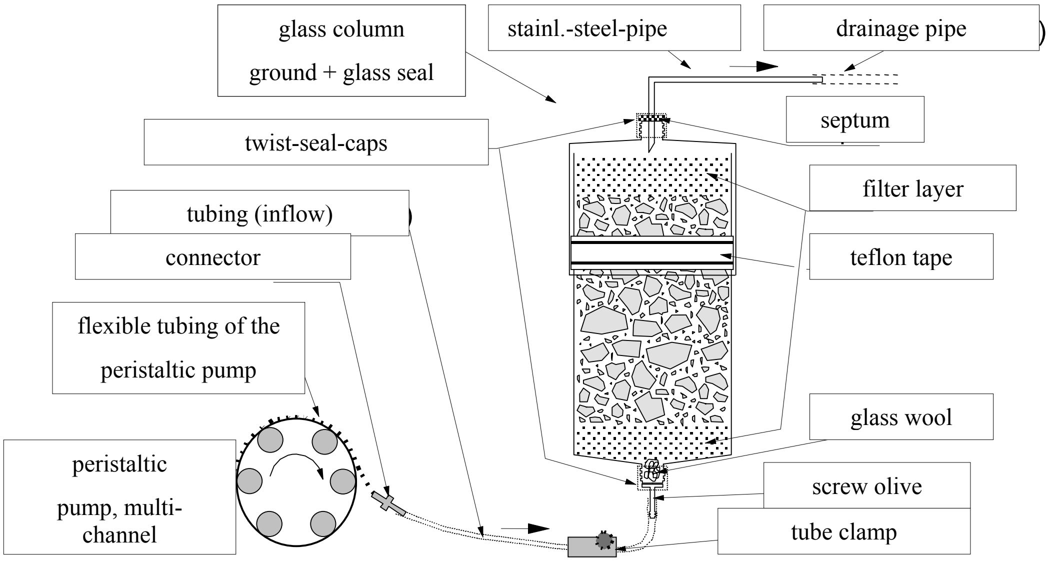


Figure A.2: *Detailed construction parts of a leaching test (schematic overview).*

The following materials have to be available in the laboratory (not being delivered)

- Peristaltic pump
- Water storage tank (degasing of water is recommended because of microbiological degradation, volume of storage tank has to be selected according to the sampling time, column should not become unsaturated)
- 1l-brown-glass-bottle, narrow bottle-neck with twist seal (DIN 28) for sampling and extraction
- For the drainage of contaminated water, when not in the stage of sampling:

- activated carbon for waste water purification
- direct drainage into the sewer system if concentrations are low
- Teflon tape

Sampling

Sampling of pore air at Værløse field site

Before sampling for organic compounds in the pore air the probes were purged to remove the air standing in the probe. The soil gas was sampled using a stainless steel fitting with Viton o-rings, which connected sorbing tubes directly to the soil gas probes consisting of a 40 cm stainless steel pipe (OD 10 mm and ID 7 mm), which was closed at the bottom and provided with 6 slits (1 mm wide) at the lower 3 cm. The pump was a SKC Personal Air Sampler (serie 222-3, SKC Ltd., UK). The sorbing tubes were packed with 50 mg Tenax TA 60/80 mesh and 200 mg Carbotrap 20/40 mesh (Sigma-Aldrich, Denmark). The air volume sucked onto the sorbing tubes varied between 5 and 200 ml depending on the expected hydrocarbon concentration level. The sorbing tubes were stored cold (4°C) until analysed.

The pore air samples for CH_4, CO_2 and O_2 analyses were sampled after purging of air standing in the probe and then 3 ml of sample was withdrawn with a syringe. The gas samples were stored in evacuated blood collection tubes (Venoject tubes, Terumo, Leuven, Belgium), and were stored cold until analysed in the laboratory using a portable Chrompack Micro GC (Middelburg, The Netherlands).

Sampling of groundwater at Værløse field site

The water samples for organic compounds were collected with a gas-tight glass syringe using vacuum from multi-level samplers (MLS). The MLS’s consisted of a solid PVC rod (D 10 mm) with 9 hard Nylon (PA 11) sampling tubes (OD 4 mm, ID 2 mm) attached on the outside with a vertical spacing of 10 cm. Each tube was screened over 5 cm. The first 20 ml sampled from each tube, which corresponds to a minimum of twice the tube volume, was discarded to ensure that no stagnant water was sampled. Thereafter samples for the organic compounds and anions composing a total of 25 ml were collected.

Pore water was sampled using a peristaltic pump. A 15 ml sampling bottle was inserted before the pump. The sampling bottle was over floated by two vial volume’s to ensure that no stagnant water was sampled.

Mobility/bioavailability tests

MICROTOX / LUMISTOX - The Microtox and Lumistox test systems are based on the use of luminiscent bacteria *Vibrio fischeri* to measure toxicity from environmental samples. When properly grown, luminiscent bacteria produce light as a by-product of their cellular respiration. Any inhibition of cellular activity (toxicity) results in a decreased rate of respiration and a corresponding decrease in the rate of luminiscence.

TOXKITS – Toxkit is the generic name for a new generation of microbiotests, which consist on the activation of the chosen test organisms, exposure to toxicant dilution series, scoring the tests parameter and determination of EC50/LC50.

CHROMOTEST - The SOS-Chromotest kit is based on a novel genetically engineered E. coli, licensed from Institute Pasteur, which measures the primary response of a cell to genotoxic damage. In just a few hours, the kit provides a clear, completely objective measurement of the genotoxicity of a sample by a simple visual appreciation of the colour obtained or by spectrophotometry using a micro-plate reader.

METPLATE - The MetPLATE kit is specific to heavy metals and it detects and measures such substances in mixtures of other toxicants. For a visual qualitative measurement, the change in colour of the test wells containing the samples is compared against the controls. For a quantitative measurement use a standard laboratory microplate reader with a 575 nm optical filter. The simplicity of the assay format provides a test method capable of analyzing multiple samples simultaneously.

METPAD - MetPad kit detects toxicity for heavy metals in aqueous solutions based on bacterial enzyme response to heavy metal presence. MetPAD does not differentiate among metals, but does detect overall heavy metal toxicity.

A 7. Selection of legal standards in European countries due to groundwater risk assessment

Regulation of soil contamination is currently based on total composition. There is no regulation based on leaching of soil, apart from the use of soil in construction works in the Dutch Building Materials Decree (1995). It is recommended to put more emphasis on leaching as it eliminates several unjustified declarations of contamination based on essentially non-leachable constituents.

Denmark:

Miljøministeriet (1999): Lov om forurenet jord (Law on polluted soil, in Danish). Lov nr 370 af 02/06/1999.

Danish Environmental Protection Agency (2002): Guidelines on Remediation of Contaminated Sites. Environmental Guidelines No. 7. 290 pages, Copenhagen, Denmark.

Danish Environmental Protection Agency (1998): Prøvetagning og analyse af jord (Sampling and analysis of soil, in Danish). Vejledning fra Miljøstyrelsen, 13.

Danish Environmental Protection Agency (2000): Kortlægning af forurenede arealer (Registration of contaminated sites, in Danish). Vejledning fra Miljøstyrelsen, 8.

Germany:

German Federal Soil Protection Law (BBodSchG), (1998): Gesetz zum Schutz des Bodens vom 17. März 1998, Bundesgesetzblatt Jahrgang 1998. Teil I, Nr.16.

German Federal Soil Protection Ordinance (BBodSchV), (1999): Bundes-Bodenschutz- und Altlastenverordnung vom 16. Juli 1999. Bundesgesetzblatt Jahrgang 1999. Teil I, Nr.36, S. 1554-1682

DIN 4047-10:1985-09, Landwirtschaftlicher Wasserbau – Begriffe - Der Boden als Pflanzenstandort.

DIN 4049-3:1994-10, Hydrologie – Teil 3: Begriffe zur quantitativen Hydrologie.

DIN 19672-1, Bodenentnahmegeräte für den Landeskulturbau - Geräte zur Entnahme von Bodenproben in ungestörter Lagerung

DIN V 38407-14, Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung - gemeinsam erfassbare Stoffgruppen (Gruppe F) – Teil 14: Bestimmung von Phenoxyalkancarbonsäuren mittels Gaschromatographie und massenspektrometrische Detektion nach Fest-Flüssig-Extraktion und Derivatisierung (F 14).

DIN 38409-18, Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung - Summarische Wirkungs- und Stoffkenngrößen (Gruppe H) – Teil 18: Bestimmung von Kohlenwasserstoffen (H 18).

DIN EN 27027, Wasserbeschaffenheit - Bestimmung der Trübung (ISO 7027: 1990); Deutsche Fassung EN 27027: 1994.

DIN EN ISO 6468, Wasserbeschaffenheit - Bestimmung ausgewählter Organochlorinsektizide, Polychlortriphenyle und Chlorbenzole - Gaschromatographisches Verfahren nach Flüssig-Flüssig-Extraktion (ISO 6468: 1996); Deutsche Fassung EN ISO 6468: 1996 (F 1).

E DIN ISO 10381 - 4, Bodenbeschaffenheit – Probenahme – Teil 4: Anleitung für das Vorgehen bei der Untersuchung natürlichen, naturnahen und Kulturstandorten (ISO/DIS 10381 – 4: 1995).

DIN ISO 11465, Bodenbeschaffenheit - Bestimmung des Trockenrückstandes und des Wassergehalts auf Grundlage der Masse - Gravimetrisches Verfahren (ISO 11465: 1993).

ISO/DIS 11074-2:1997, Soil quality – Vocabulary – Part 2: Terms and definitions relating to sampling.

ISO TR 11046, Soil quality - Determination of mineral oil content - Method by infrared spectrometry and gas chromatographic method.

ISO/CD 15009, Soil quality - Gas-chromatographic determination of the content of volatile aromatic hydrocarbons - Purge and trap method with thermal desorption.

DIN V 19736: Bodenbeschaffenheit: Ableitung von Konzentrationen organischer Schadstoffe im Bodenwasser

Pre-standard: (Soil quality: Derivation of concentrations of organic pollutants in soil water

The Netherlands:

PrEN 14429: pH static leaching test. The method is being standardized in two experimental modes (initial acid/base addition and continuous pH control) by CEN/TC 292 Working Group 6.

PrEN14405: Column leaching test. With similarities to NEN 7343, developed at European level in CEN/TC 292/WG6. In ISO TC 190/SC7/WG 6 a percolation leaching test similar to PrEN 14405 is in development (ISO/AWI 21269-3). This procedure addresses both inorganic and organic contaminants.

NEN 7345: Tank leach test

NVN 7347 (Dutch pre-standard): Compacted granular leaching test

EN 12457. CEN/TC 292: Compliance test for granular materials. In ISO TC 190/SC7/WG 6 two batch leaching tests similar to EN 12457 Part 1 and 2 are in development (ISO/AWI 21269 – 1and ISO/AWI 21269 – 2). The latter focus on inorganic and organic contaminants.

ENV 12920:1998, (CEN/TC292/WG6, 1999): Characterization of waste -- Methodology for the determination of the leaching behaviour of waste under specific conditions.

Draft prEN XXXX: Characterization of waste -- Determination of dry residue and water content.

Draft prEN XXXX: Characterization of waste -- Sampling strategy -. Guide to the preparation of a plan for liquid and granular waste materials, including paste-like materials and sludges.

EN 27888:1993: Water quality -- Determination of electrical conductivity.

EN ISO 5667-3:1995: Water quality -- Sampling -- Part 3: Guidance on the preservation and handling of samples.

ENV 12506:2000: Characterization of waste -- Chemical analysis of eluates -- Determination of pH, As, Cd, Cr^{vi}, Cu, Ni, Pb, Zn, Cl, NO_2, SO_4.

ENV 13370:2001: Characterization of waste – Analysis of eluates – Determination of Ammonium – N, AOX, conductivity, Hg, phenol index, TOC, CN^- easily liberatable, F.

Spain:

Ley 10/1998 de Residuos (Spanish Law 10/1998 of Wastes)

Ley 3/1998 General de Protección del Medio Ambiente del País Vasco (Generic Law 3/1998 of Environment Protection of the Basque Country)

Ley 29/1985 de Aguas (Spanish Law 29/1985 of Water)

Real Decreto 849/1986, Reglamento del Dominio Público Hidráulico (Royal Decree 849/1986 for the Regulation of the Hydraulic Public Domain)

Real Decreto 2618/1986, por el que se aprueban las medidas referentes a acuíferos subterráneos al amparo del artículo 56 de la Ley de Aguas (Royal Decree 2618/1986 for the approval of measures in groundwaters under Article 56 of Spanish Law of Water)

Real Decreto 927/1988, Reglamento de la Administración Pública del Agua y de la Planificación Hidrológica – (Royal Decree 927/1988 Regulation of the Water Public Administration and Hydrologic Planning)

Orden Ministerial de 16 de diciembre de 1988 sobre métodos y frecuencias de análisis o de inspección de las aguas continentales que requieran protección o mejora para el desarrollo de la vida piscícola. (Ministerial Order of December 16th, 1988, concerning methods and frecuency of the analysis or monitoring of continental waters for the protection or enhancement of development of fishing life)

Real Decreto 995/2000, por el que se fijan objetivos de calidad para determinadas sustancias contaminantes y se modifica el Reglamento de Dominio Público Hidráulico (Royal Decree 995/2000, for target values for contaminants, which modifies Royal Decree 849/1986 for the Regulation of the Hydraulic Public Domain)