



## Monitored natural attenuation of chlorinated solvents: assessment of potential and limitations

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### Abstract

Chlorinated solvent contaminations in groundwater and soil are a widespread problem. Their remediation either by active and/or passive measures is complicated though, due to their characteristic features of long plumes and DNAPL. In this study Monitored Natural Attenuation (MNA) is evaluated regarding its applicability to remediate chlorinated solvent sites. At first a short overview of legal requirements is given, by whose means the efficiency of MNA is supposed to be demonstrated and assessed. Thereby the focus is set on the circumstances in the United States and Germany, as in the first MNA is applied as remediation option, whereas in the latter implementation and definition of MNA is under discussion. Based on criteria given by several German guidelines investigation methods and suitable parameters are discussed with the objective to evaluate their potential and limitations to demonstrate MNA at a chlorinated solvent site. Regarding the description of source location/inventory and source emission the legal requirements cannot be accomplished mainly because of missing methods. With regard to the characterization of plume migration, and evaluation of the efficiency of NA processes the combination of hydrogeochemical data and model approaches can accomplish most of the legal requirements. Applicability of microbiological and isotope methods is limited which is also reflected by evaluation of field studies, where these methods have been used at less than 10% of the sites. With regard to chlorinated solvents current German guidelines should be modified to enable the feasible application of MNA as an alternative or additional remediation option.

### Introduction

Chlorinated solvents (CAH) have been widely used as degreasing agents and solvents in the chemical industry and in metal processing. As a consequence of improper use, doubtful waste disposal and leaking storage facilities perchloroethylene (PCE) and trichloroethylene (TCE) represent a major groundwater and soil pollutant. Their presence in the environment is of concern, as chlorinated ethenes are known or suspected carcinogens. Leaving their toxicity apart, the handling of chlorinated solvent contaminations and plumes is a demanding task as CAH are very mobile and persistent. Because of their physico-chemical properties they can

dissolve in groundwater, volatilise in the unsaturated zone, sorb onto soil matrix or organic material or exist as dense non-aqueous-phase-liquids (DNAPL). Mean lengths of CAH plumes range from 300 m ( $n = 88$ , Newell et al. 1990 cited in Wiedemeier et al. 1999) to 1500 m ( $n = 107$ , Teutsch et al. 1997). They exceed BTEX or PAH plumes by a factor of 2–5, which indicates their potential threat to distant receptors and pristine groundwater zones.

Practical experience in active approaches like pump-and-treat (P&T) indicate that the cleanup process is lengthy, expensive and even in-effective. P&T operations generally last between 5 and 10 years (FRTR 2003; US EPA 2001). Median

annual operating costs were estimated at 260,000 US\$ for a treated groundwater volume of 115,500 m<sup>3</sup> year<sup>-1</sup> ( $n = 32$ , EPA 2001). Evaluation of P&T efficiency (NRC 1994) showed that though in 23 of 34 cases containment was achieved, cleanup goals have been failed in 90% of the cases. Removal of the contaminants from the aquifer is e.g. slowed by kinetic limitations, thereby increasing both the time required to achieve cleanup and the total volume of water that must be extracted to flush the contaminated zone. Thus pumping is often ceased before all of the contaminant is removed, and desorption of CAH in groundwater continues (Mackay & Cherry 1989; Rifai et al. 1997).

For this reason Monitored Natural Attenuation (MNA) has been discussed as a promising, cost-effective additional or alternative remediation option for CAH plumes. Though economic calculations argue for MNA (Ellis 1997; Imbrigiotta et al. 1997), and regulatory acceptance of MNA in general is increasing, MNA with respect to chlorinated solvents is still a controversially discussed topic. Despite the fact that knowledge about their degradation pathways has improved a lot, large plume dimensions and complex degradation mechanisms complicate demonstration of MNA in the field. However, independent from the remediation technologies chosen, site investigation and remediation of CAH will in general be hampered by the difficulty of locating source and/or DNAPL and by characterizing long plumes in heterogeneous aquifers.

The aim of this paper is to give a brief overview of considerations and options for regulatory acceptance of NA. Thereby a focus is set on German administrative requirements as in Germany implementation of MNA is in the works. Afterwards a general overview of current site characterization and monitoring methods is provided in order to assess the potential and limitations of available techniques to demonstrate MNA. In doing so the practical options are compared to the legal requirements focussing on the contaminant group of chlorinated solvents. Finally data from chlorinated solvent MNA field investigations are compiled and assessed in respect of the actual investigation procedures for case studies. This aims to propose MNA investigation and assessment concepts which are from a scientific point of view feasible for an application of MNA in Germany.

## Legal criteria to assess MNA at chlorinated solvent sites

In contrast to the United States, where MNA is defined and accepted as 'one option that should be evaluated with other applicable remedies' (US EPA 1999), MNA has so far neither been defined nor regulated by law in Germany. The remediation of abandoned sites in general is ruled by the 'Bundesbodenschutzgesetz/-verordnung' (German Federal Soil Protection Act), additionally groundwater issues are subject to the 'Wasserhaushaltsgesetz' (Federal Water Act). Hence, the German federal states and their legal authorities are responsible for handling contaminated groundwater sites. Various legal authorities are currently developing guidelines and recommendations (ITVA 2003; LfU Bayern 2003; LUG Hessen 2003) outlining under which circumstances MNA could be considered as an additional or subsequent option to active measures in Germany.

Use of MNA demands sufficient protection of potential receptors and the environment. In addition, contaminated groundwater and soil have to be cleaned up by preferably irreversible degradation processes (ITVA 2003; US EPA 1999). In the United States, Great Britain or the Netherlands MNA relies on a risk-based approach regarding potential receptors (Rügner et al. 2003; Small 1998; Ward 1997). Assessment of MNA includes the collection of site characterization data, the development of a site conceptual model and the evaluation of MNA efficiency by a 'three lines of evidence concept' (US EPA 1999). This concept includes (1) proof of decreasing contaminant mass and/or concentration over time, (2) indirect proof of types of NA processes by hydrogeological and geochemical data and (3) direct demonstration of particular NA processes by field or microcosm studies (described in several protocols and reports: AFCEE 1999; Carey et al. 2000; ITRC & RTDF 1999; Sinke & Hecho 1999; US EPA 1998). Scoring systems to evaluate NA processes proposed by the US EPA Technical Protocol (1998) are 'susceptible to misuse' (NRC 2000), though Clement et al. (2002) stated that 'if applied carefully, the method does provide a means for systematically assembling a diverse set of footprints in a compact format'. The NRC (2000) recommends a weight-of-evidence approach, measuring several 'footprints', for demonstrating the mechanisms

responsible for the observed contaminant losses. 'Footprints' are defined as decreases in contaminant and electron donor concentrations or alkalinity corresponding with increases in metabolite concentrations or production of inorganic carbon. Increasing chloride concentrations can often not be detected against high background levels. Distribution maps of other electron acceptor, contaminant and metabolite concentrations provide information about the relative importance of the respective terminal electron accepting processes. Documentation of such cause-and-effect linkages is proposed by (1) the creation of a conceptual model with characterization of the flow system, and delineating the contaminant source and plume, (2) the quantification of NA processes using mass balances and modelling, and (3) the establishment of a long-term monitoring program (NRC 2000).

In Germany remediation goals for contaminated groundwater are based on legal limit or threshold concepts in contrast to the US risk-based approach. Application of MNA would require that groundwater contaminations are 'tolerated' for a defined and acceptable period considering the 'Verhältnismäßigkeitsprinzip' ('principle of comparativeness') and future use of the site (ITVA 2003; Willand & Großmann 2002). In this context an 'acceptable time period' is defined according to the objectives given by the European Groundwater Directive (ITVA 2003) or no longer than 10–30 years (LUG Hessen 2003). MNA can be considered for 'locally restricted' plumes, where 'minor loads' are expected, or when plume concentrations do not exceed defined 'Geringfügigkeitsschwellenwerte' ('insignificance threshold values'). Definitions of 'locally restricted', 'minor loads' and the 'threshold values' are given in some federal law acts (Bannick et al. 2000; LUG Hessen 2003; Müller 2001; Rügner & Teutsch 2002), however details where and how concentrations have to be measured are partly missing. Source control is an optional pre-condition subject to aspects of comparativeness, whereas some US regulations recommend that 'assessment of NA as a remedy should take place after source control actions are complete' (Wisconsin DNR 2003). Where reasonable, active measures have to be preferred, thus MNA is regarded as an additional or subsequent procedure rather than a sole remediation measure. MNA is

not accepted in karstic, structured and/or fractured rock aquifers, at sites which demand for an immediate remediation action, where receptors are directly endangered and in drinking water reserves (LUG Hessen 2003). The criteria required to consider MNA according to German guidelines are summarized in Table 1 and classified as source, plume inventory and NA processes.

### Available techniques to demonstrate legal requirements

#### Source

Identification of source position and inventory (Table 1) could be deduced from historical data. However they are often incomplete, do not include information about leakages, or migration of residual DNAPL thus their information content is restricted. Source location/inventory can be investigated by means of partitioning tracer tests. To date these approaches are on the status to find suitable tracers, and to scale results from laboratory models to length and time scales of field applications (Brooks et al. 2002; Imhoff et al. 2003; Istok et al. 2002). Required that source location is known, immission pump tests and direct-push

Table 1. Requirements and criteria to consider MNA as a remedy option according to existing German protocols and guidelines

<i>Source</i>
–Identification of position of source/DNAPL <sup>a</sup>
–Small source inventory <sup>b</sup>
–No dislocation of contaminants in deeper aquifers <sup>b,c</sup>
–Source removal (optional) <sup>b,d</sup>
<i>Plume inventory and dimension</i>
–No toxic intermediates <sup>b</sup>
–Plume stable or regressing <sup>b,d</sup>
–No harm of further receptors <sup>b,d</sup>
–Durable reduction of contaminant load, no dilution <sup>b,d</sup>
<i>NA processes in the plume</i>
–Qualitative and quantitative evidence <sup>b,c,d</sup>
–Determination of degradation rates and microbial activity <sup>b</sup>

<sup>a</sup>Martus & Püttmann (2000).

<sup>b</sup>LUG Hessen (2003).

<sup>c</sup>LFU Bayern (2003).

<sup>d</sup>ITVA (2003).

techniques can be used to determine source inventory, yet these techniques have been hardly applied at CAH sites.

Migration of DNAPL in deeper parts of the aquifer (Table 1) can be a priori not ruled out, as DNAPL due to their higher density migrate downwards as long as gravity are equal to capillary forces or migration is hindered by an impermeable aquitard. Identification of DNAPL can be investigated by drilling, implying the risk that DNAPL are given new pathways, which would result in a man-made undesired dislocation of DNAPL.

If hydraulic protection actions are not possible, source removal in terms of mobilisation of the residual DNAPL can be achieved by physico-chemical approaches. They include e.g. flushing of DNAPL with surfactants, linker molecules or co-solvent-air-flooding (e.g. Acosta et al. 2002; Jayanti et al. 2002; Jeong et al. 2002). Density modification is achieved by flushing the subsurface with emulsions to modify buoyancy forces of DNAPL (Ramsburg & Pennell 2002; Ramsburg et al. 2003; Yan et al. 2003). Though most of these new approaches have so far been restricted to laboratory experiments, the results indicate large emission rates at the beginning of the DNAPL displacement but give few information on long-term emission scales. Enhanced Natural Attenuation (ENA) by biochemical options aim to stimulate *in situ* degradation and mobilization by the injection of catalyzing substrates and/or electron donors like e.g. potassium permanganate, Hydrogen Release Compounds, lactate, or acetate (Conrad et al. 2002; McNab et al. 2000; Yang & McCarty 2002). Efficiency of biostimulation of PCE, TCE and *cis*-DCE degradation using permanganate was demonstrated by carbon isotope fractionation in field and laboratory studies (Hunkeler et al. 2003; Poulson & Naraoka 2002). The findings that CAH degrading cultures show no or few inhibitory effects under saturated CAH concentrations enable bioaugmentation approaches where enriched cultures are inoculated in the source zone (Adamson et al. 2003; Yang & McCarty 2000). Field studies on bioaugmentation indicate that dechlorination beyond *cis*-DCE may be limited to regions downgradient of the source zone, but might be reached in combination with biostimulation (Adamson et al. 2003; Ellis et al. 2000; Lendvay et al. 2003; Major et al. 2002; Song

et al. 2002). Consequently bioaugmentation increases source emission at the beginning. On time scales of years emission rates decrease and plume lengths are shortened. The efficiency of bioaugmentation depends on several boundary conditions like intrinsic microorganism community structures, available electron donors, competitive reactions, bio-clogging and distribution and mass of CAHs in the source (Chu et al. 2003). Effective applicability for large sources or pools is suggested to be unlikely.

In summary rather none of the legal requirements relating to the source (Table 1) can be fulfilled. Identification of source position is if at all most realistic at newly detected contaminations or accidents, therefore investigation of source inventory is also limited. Source removal *via* ENA increases source emission on short time scales but is supposed to decrease emission rates on the long-term, though final conclusions are to be validated. Source emission is the relevant feature to predict plume-lifetime and thus duration of MNA. Yet knowledge about source emission, though essential, should not be handled as a compulsory feature to accept MNA, because technical and scientific investigation methods are limited.

#### *Plume inventory and dimension*

The generation of toxic intermediates (Table 1) cannot be excluded for chlorinated solvent plumes. The production and further degradation of the most toxic intermediate VC depends on the prevailing redox conditions and present microorganisms. Microbial reductive dechlorination of VC is dependent on the dissolved VC concentration and likely to be inefficient under relatively oxidized field conditions or at low VC concentrations (Bradley 2003). The aerobic biodegradation is widespread in chloro-ethene-contaminated environments (Coleman et al. 2002a).

The knowledge about the existence of a stable plume resulting in no harm of distant receptors (Table 1) would demand a detailed mapping of the plume migration and its fringes in particular. The number and density of point measurements are increased by multi-level systems or supplemented by comparatively cheap direct-push investigations. More data generally allow statistical approaches in data interpretation and the evaluation of bias due to interpolation. Verification of a stable plume by

means of long-term monitoring wells and compliance wells (US EPA 1998; Wiedemeier et al. 1997) does require the knowledge that these wells are placed adequately to detect behaviour and movement of the plume, which is precisely the topic of monitoring. In case of organic chemicals, stable or decreasing concentrations observed over a space of time at a specific monitoring well can simply be the result of a migrating plume and/or the well placed outside the plume-center line, at the fringe or even outside of the plume. Consequently concentration measurements might indicate a stable plume, whereas the actual plume is not. At sites characterized with varying flow regimes and bearing in mind that average CAH plume lengths are 300–1500 m it becomes obvious that a detailed plume characterization even with good historical data information cannot be achieved by few wells. Database studies by McNab et al. (1999) showed that of 35 TCE plumes in total with lengths > 300 m, only four were characterized by less than 10 wells, whereas at all other sites 10–50 wells were installed. At a BTEX test-site, plume migration and dimension (> 500 m) could not be determined, based on a monitoring period of 3 years and a network consisting in the end of 77 wells (Wachter & Dahmke in press). Though the regulatory requirements demand for plume stability, a stable plume is suggested to be not essential for an acceptance of MNA as long as there is no receptor directly endangered.

Durable reduction of contaminant load (Table 1) is achieved by irreversible NA processes, i.e. degradation. Dilution effects can be differentiated from degradation processes by means of isotope measurements or immission pump tests (IPT), in the latter contaminant loads and mass fluxes through transects are determined (Ptak et al. 2000; Teutsch et al. 2000). Yet IPT have the disadvantage of perturbing the intrinsic flow-regime, dissolved electron donors required for CAH degradation are withdrawn, and the natural biotic system in general is mutilated. Furthermore few knowledge exists about recreation times in case of CAH sites. In addition positioning of the wells, calibration of adequate pumping rates and pumping times is tricky. IPT have been applied at several BTEX, PAH, or NH<sub>4</sub> sites (Bockelmann 2002; Rügner et al., in press), in contrast applications at CAH sites are in the beginning (Grandel & Dahmke 2003). As IPT is currently the main

technique to determine mass loads, a compulsory demand for determination of load reduction might induce the unrequested effect of diminishing NA processes caused by the investigation method.

#### *NA processes in the plume*

The likelihood and efficiency of NA processes is investigated by geochemical, microbiological, and isotopic parameters and modelling approaches. Determination of degradation rates and estimation of microbial activity is also based on these parameters determined either in the field or in laboratory studies. Preliminary to the assessment of the various methods which are used to determine the parameters NA processes affecting CAH are briefly summarized.

#### *NA processes relevant for chlorinated ethenes*

Natural attenuation processes which irreversibly reduce CAH concentrations in the groundwater are microbiological and abiotic degradation. The higher chlorinated solvents PCE and TCE are degraded *via* reductive dehalogenation to lesser chlorinated ethenes and ethene (Drzyzga & Gotschal 2002; Ellis et al. 2000; Fennell et al. 2001; Löffler et al. 2000; Richardson et al. 2002; Tandoi et al. 1994). A complete degradation of PCE to ethene has only been reported for the pure culture of *Dehalococcoides ethenogenes* (Maymó-Gatell et al. 1997). The predominant biological degradation product of PCE and TCE is *cis*-1,2-DCE, whereas the isomers *trans*-1,2-DCE and 1,1-DCE are produced to a much lesser extent. VC and *cis*-DCE are degraded either *via* reductive dehalogenation (Bradley & Chapelle 1997, 1999a, b, 2000a; Flynn et al. 2000; Maymó-Gatell et al. 2001), *via* cometabolism or by aerobic mineralization (Bradley & Chapelle 1998, 2000b; Coleman et al. 2002b; Verce et al. 2000, 2001, 2002). For an up-to-date overview see Bradley (2003). Efficiency of biodegradation in general depends on (1) availability of the electron donor, (2) competition of other terminal electron acceptors, (3) macro- and micronutrients, and (4) present bacterial communities and their enzyme systems. On a field scale though degradation is mainly affected by transport and mixing processes influencing supply of electron donors and electron acceptors.

The main abiotic degradation processes are substitution and dehydrohalogenation (Vogel

et al. 1987). Acetylene is the main product of TCE and PCE transformation by iron sulphide, pyrite or magnetite (Butler & Hayes 1999; Lee & Batchelor 2002), consequently acetylene could be used as an indicator of abiotic transformation processes. However production of *cis*-DCE and VC has also been observed from TCE transformation by iron sulphide under pH-values of 7.3–8.3, whereas pH-values of 9.3 in the batch experiment resulted in a 96% production of acetylene (Butler & Hayes 2001). Apart from solution composition (particularly pH) abiotic transformation rates and products mainly depend on the type of iron-bearing soil minerals (Hofstetter et al. 2003). In lab experiments green rust ( $\text{GR}_{\text{so}_4}$ ) revealed the greatest reductive capacity for PCE, followed by magnetite, pyrite, biotite, montmorillonite and vermiculite (Lee & Batchelor 2003). Though under natural conditions abiotic transformation with half-life values between 0.9 and 2.5 years for TCE and 0.7 and 6 years for PCE (Vogel et al. 1987) is slow compared to bioremediation rates (half-life values of 0.01 year for TCE or 0.04 year for PCE from Suarez & Rifai 1999) it still can be significant in time scales associated to groundwater movement. Beyond abiotic transformation can be accelerated by the activity of biologically derived extra cellular enzymes (Roden 2003; Vogel et al. 1987).

In contrast to degradation, adsorption and desorption of CAH in subsurface soils are reversible NA processes. Time scales of desorption from a solid matrix are estimated to be < 1 to 10 years, whereas CAH dissolution from DNAPL is estimated to take 1 to > 10 years for smear zones and > 10–1000 years for pools (Grathwohl 2001). Despite the fact that most of the dissolution processes are theoretically understood, transfer into field application still leaves a lot of unresolved issues. Dissolution rates in the field are estimated to be slower than calculated values as modelling approaches are limited by unknown boundary conditions i.e. site-specific rate limitations in DNAPL dissolution, micro scale irregularities of the DNAPL pool and/or the presence of microlayers (Khachikian & Harmon 2000; NRC 1994). These results suggest further on that the existence of DNAPL cannot be excluded in contaminant plumes dominated by concentrations several orders of magnitude less than the aqueous solubility (Chrysikopoulos et al. 2000). Sorption effects ex-

pressed by retardation factors have been calculated to be 1.3 (PCE), 1.2 (TCE), and 1.1 (DCE), respectively (Witt et al. 2002) given a soil organic carbon content of  $f_{\text{oc}} = 0.00025$ . Given a higher organic carbon content ( $f_{\text{oc}} = 0.0039$ ) Clement et al. (2002) determined retardation coefficients for the same contaminants of 6.5, 4.0, and 2.4, respectively. Consequently, if retardation factors reach values > 1, which is likely for higher soil organic carbon contents, sorption processes have to be considered for evaluation of MNA.

#### *Hydrogeochemical parameters*

Hydrogeochemical parameters include (1) classical parameters to characterize redox conditions (dissolved oxygen, nitrate, ammonium, iron, manganese, sulphate, methane), (2) contaminant concentrations, (3) concentrations of metabolites and end-products (ethene, ethane, acetylene, chloride,  $\text{CO}_2$ , alkalinity), (4) natural or anthropogenic organic carbon sources or electron donors determined e.g. as DOC, BTEX, acetate, pyruvate,  $\text{H}_2$ , and (5) solid phases of iron or manganese.

Direct electrochemical measurements with redox sensors and a straightforward interpretation of the redox potential is complicated by slow electrode kinetics and the lack of internal equilibrium of redox processes in groundwater plumes (Christensen et al. 2000). Therefore redox conditions are often determined indirectly *via* redox-sensitive compounds in the groundwater (see parameters mentioned above (1)). Reliable solid fraction analyses depend heavily on representative sediment samples, where the reactive species have to be kept intact during sampling, handling and storage (Christensen et al. 2000).

Different levels of fermentation products e.g. volatile fatty acids, acetate or  $\text{H}_2$  are discussed as indicators for redox processes in different sediment types (Christensen et al. 2000). Theoretical thermodynamic considerations (Hoehler et al. 1998; Lovley & Goodwin 1988) suggest that, at steady-state conditions,  $\text{H}_2$  concentrations are primarily dependent upon the physiological characteristics of the microorganisms consuming the  $\text{H}_2$  and those catalyzing  $\text{H}_2$  oxidation, with the reduction of a terminal electron acceptor (TEA). Various laboratory studies examined the influence of electron donors like lactate, propionate, methanol, and  $\text{H}_2$  as hydrogen donors for reductive dehalogenation activities (Ballaprada et al. 1997; Carr

& Hughes 1998; Fennell et al. 1997; He et al. 2002; Maymó-Gatell et al. 1995).  $H_2$  seems to be the preferred ultimate electron donor for dechlorinating bacteria, and can be also produced by syntrophic microorganisms during fermentation processes of more complex initial electron donor substrates like other organic contaminants (e.g. BTEX). Such preference however leads to competition for available  $H_2$  between dechlorinators and other anaerobic bacteria like e.g. methanogenic bacteria. The reduction potential of a TEA process defines that process's theoretical  $H_2$  threshold, which is inversely related to the Gibbs free energy change of a reaction. Laboratory experiments indicate that for  $H_2$  concentrations ranging between 0.3 and 2.5 nM reductive dehalogenation of PCE, TCE and *cis*-DCE is the favourable electron accepting reaction (Ballaprada et al. 1997; Kassenga et al. 2004; Löffler et al. 1999; Mazur & Jones 2001; Mazur et al. 2003; Smatlak et al. 1996; Yang & McCarty 1998). Though these results sound promising, the use of  $H_2$ , as an indicative parameter to account for reductive dehalogenation processes under field conditions is restricted. Field measurements are biased and affected by different pumping equipment (Chapelle et al. 1997; Heimann 2003) as well as the material and age of the well (Bjerg et al. 1997). In addition deduction of TEA processes by means of  $H_2$  concentrations is not always in coincidence with the other redox parameters (Chapelle et al. 1996; Heimann 2003; Richmond et al. 2001).

In conclusion the evaluation of redox conditions is often a prerequisite for understanding the behaviour of pollutants in a plume. Most likely the redox activity in the field is limited by one or more factors, such as mass transfer, availability of electron donors and acceptors, the thermodynamic energetics of the processes, and microbial kinetics (Christensen et al. 2000). NA processes can be qualitatively assessed by combining redox measurements with changes in contaminant and metabolite concentrations. Mass budgeting which is according to NRC (2000) regarded to deliver relative rates which natural attenuation processes are important and which not refers to having all rates on a common mass-per-time basis. This is hardly achieved for all necessary compounds on a field scale and is also hampered by artefacts while sampling volatile compounds in water or gas

phases or sampling reactive solid fractions. Apart from biases during sampling analysis of dissolved substances (i.e. organic contaminants, metabolites, oxygen etc.) follows standard procedures, whereas the measurement of the redox potential is not straightforward. The establishment of mass balances thus has to our knowledge so far not been applied on a numerical model basis at a chlorinated solvent site.

#### *Microbiological parameters*

Microbiological methods involve counting methods, cultivation techniques and cultivation-independent methods such as biomarkers, gene probes or DNA fingerprinting (Azadpour-Keeley et al. 1999; Röling & Van Verseveld 2002). Cell count methods may indicate constant physical properties, whereas the microbial activity is not (Röling & Van Verseveld 2002). Microcosm studies aim to identify process mechanisms and determine degradation rates. Despite the large amount of determined degradation rates (summarized by Suarez & Rifai 1999,  $n = 138$ ) their practical use is crucial. On the one hand because of limited comparativeness in consequence of different experimental approaches (batch, column, etc.) and due to restricted transferability to field conditions. Cultivation-independent methods are applied to identify enzymes, microbial species and community structures of CAH degrading bacteria (Richardson et al. 2002; Tani et al. 2002; Vercé et al. 2000). Though possibilities to identify bacteria capable of degrading CAH increases (Holiger & Schraa 1994; Middeldorp et al. 1999) at present 16S rRNA techniques are insufficient to distinguish between dehalogenating bacteria populations (e.g. Dehalococcoides) with different dechlorination activities and, consequently are a poor means of assessing the *in situ* potential for complete reductive dechlorination (Bradley 2003 and citations within).

In summary microbial methods are restricted to demonstrate the presence of microbial species within groundwater samples. Functional correlations between their presence and degradation activity cannot be established. Thus microbial studies being also very time consuming can serve as additional information supplementing results from hydrogeochemical investigations but are not appropriate for intensive field investigations or as sole parameter to evaluate NA processes. This is

also represented by their proportion in actual case studies. Compared to hydrochemical analyses microcosm studies and cultivation independent methods are usually carried out at samples deriving from 10% to 25% of the investigation wells (see Table 3).

#### *Isotope measurements*

Laboratory studies have shown that biological CAH degradation can involve reproducible kinetic isotopic effects, producing systematic changes in the  $\delta^{13}\text{C}$  values of the residual contaminant (Barth et al. 2002; Bloom et al. 2000; Hunkeler et al. 1999, 2002; Sherwood-Lollar et al. 2001; Slater et al. 2001). These studies also revealed that the magnitude of fractionation decreases with increasing degree of chlorination of the chlorinated ethene.

Utilisation of isotope data requires isotopic effects large enough to be differentiated from background signals and analytical uncertainties, which range between 0.04‰ and 0.09‰ depending on the analytical system (Hunkeler et al. 1999; Kirtland et al. 2003). Isotopic enrichment in the residual contaminant relative to its initial isotopic composition were reported of up to 5–6‰ for PCE (Hunkeler et al. 1999; Slater et al. 2001), up to 14‰ for TCE (Bloom et al. 2000; Hunkeler et al. 1999; Slater et al. 2001), and up to 19.9‰ for *cis*-DCE (Hunkeler et al. 2002). For aerobically mineralized TCE an enrichment factor of 18.2–20.7‰ was reported (Barth et al. 2002), indicating typical isotopic fractionations for specific enzymatic mechanisms that can help to differentiate between degradation processes.

Table 2. Needed input parameters for the analytical model BIOCHLOR (Aziz et al. 2000a)

Parameter	Data source
<b>A – Hydrogeological data</b>	
(1) hydraulic conductivity, hydraulic gradient	Measured
(2) effective porosity	Measured
(3) seepage velocity	Deduced from the 1–2
<b>B – Dispersivity</b>	
(4) not optional	Provided by BIOCHLOR, literature
<b>C – Adsorption</b>	
(5) bulk density	Measured, literature
(6) partition coefficient	Measured, literature
(7) fractionation org. carbon	Measured, literature
(8) retardation of each constituent	Calculated from 5–8, 2
<b>D – Biotransformation</b>	
(9) first order decay rate	Measured (lab, field); deduced from half-life values
(10) abiotic first order rates	Mainly literature
(11) yield	Provided by BIOCHLOR for CAH, literature
<b>E – Source data</b>	
(12) source area concentration	Measured in source area monitoring wells
(13) source area width	Measured in source area monitoring wells
(14) source thickness in sat. zone	Measured in source area monitoring wells
<b>F – Field data</b>	
(15) monitoring wells in plume centerline <i>wells distributed in and around the plume</i>	CAH, metabolite, end-product concentrations (measured) <i>CAH, metabolite, end-product concentrations, redox parameters, electron donors, <math>\text{H}_2</math> (measured) degradation rates, Monod-parameters, oxidation-, reduction capacity (deduced)</i>

Additional parameters needed for numerical model simulations are marked in italic.



Under field conditions isotopic enrichment is determined by comparing the isotope signals from a sample near the source to a sample further downstream. Determination of the precursor  $\delta^{13}\text{C}$  signal, which is essential to calculate the enrichment factor, is hampered when waters originate from different sources. Identification by means of literature data are less useful as precursor signals vary widely  $\pm 60\text{‰}$  (Kirtland et al. 2003). In this context measurement of  $^{14}\text{C}\text{-CO}_2$  is suggested as a promising method to differentiate between contaminant and natural carbon sources, because of their vast differences in  $^{14}\text{C}$  activity (Kirtland et al. 2003). Furthermore dechlorination products could be distinguish from manufactured PCE and TCE by different hydrogen isotope values, as during degradation the  $\delta^2\text{H}$  value of surrounding water is incorporated (Shouakar-Stash et al. 2003).

The results reveal that the use of isotope signals needs extended 'background' knowledge which is hardly provided by literature data regarding the chlorinated solvents. Therefore extensive and cost-effective isotope analyses are required to enable a quantitative assessment of NA processes, which is

rather unrealistic for most site investigations. Isotopic investigations have been reported for only 3 pilot studies (Kirtland et al. 2003; Sherwood-Lollar et al. 2001; Vieth et al. 2002). Enrichment factors determined in the field and fractionation factors from the laboratory were used to estimate biodegradation rates of 41–66% for TCE (Sherwood-Lollar et al. 2001), and 46–87% for PCE (Vieth et al. 2002), respectively for wells downstream relative to the source well. The results indicate, that isotope measurements, though interesting from a scientific point of view, are unlikely to be applied as a standard method for field investigations.

### Modelling

Model approaches are the relevant tools to quantify NA processes and gain prognoses on plume migration and plume-lifetime. Depending on site conditions, available data and remediation goals mere degradation rates, simplified analytical or complex numerical models (e.g. MTD3, RTD3, Bioplume 3, TBC) are applied.

Table 3. Kind of data used for evaluation of MNA

	McNab et al. (1999)	Aziz et al. (2000a, b)	Additional studies
Number of sites	65	24	11
Kind of data mainly determined/ compiled	Hydrogeochemical <sup>a</sup> , cont. concentration, plume dimension	Hydrogeochemical <sup>a</sup> , cont. concentration, plume dimension, redox parameters, electron donors	Hydrogeochemical <sup>a</sup> , cont. concentration, plume dimension, redox parameters, electron donor
Microbiological data: including = > cell counts and/or micro- cosm studies = > and/or cultivation independent methods	No	No	At 7 sites  At 6 sites <sup>b</sup>  At 4 sites <sup>c</sup>
Isotope methods	No	No	At 2 sites <sup>d</sup>
Occuring of dechlorination (site percentage or site number)	At 30% of sites to TCE At 30% of sites to <i>cis</i> -DCE	At 25% of sites incomplete	6 sites – yes 4 sites – partial, 1 site – no

<sup>a</sup> Parameters under A, B, C in Table 2.

<sup>b</sup> Bradley & Chapelle (1997), Davis et al. (2002), Skubal et al. (2001), Richmond et al. (2001), Lenczewski et al. (2003), Fennell et al. (2001) Clement et al. (2002).

<sup>c</sup> Davis et al. (2002), Hohnstock-Ashe et al. (2001), Lenczewski et al. (2003), Fennell et al. (2001).

<sup>d</sup> Sherwood-Lollar et al. (2001), Hohnstock-Ashe (2001).

First-order rate constants represent the 'simplest' approach to quantify NA processes allowing to estimate plume attenuation and duration (Newell et al. 2002). They are calculated as concentrations versus time or distance rate constants. The analytical model BIOCHLOR developed for CAH is a simplified prognostic tool. It aims to determine how far a dissolved CAH plume will extend if no engineered controls or source area reduction measures are implemented (Aziz et al. 2000a). The required input parameters are listed in Table 2. BIOCHLOR has the limitations of assuming simple groundwater flow conditions, uniform hydrogeologic and environmental conditions over the entire model area and is primarily designed for sequential reductive dehalogenation (Aziz et al. 2000a; Clement et al. 2002). Besides these restrictions it serves as a suitable screening tool to determine if NA is occurring at sufficient rates, or as part of a conceptual model. In this context it was used to determine NA capacity at various sites (Aziz et al. 2000b; Bradley & Chapelle 1998).

Numerical model approaches become necessary at large sites characterized by varying flow, complex biogeochemical conditions or contaminant mixtures, which is valid for most of the CAH sites. Numerical simulations consider multiple transport and reaction processes for which rates or properties may vary spatially or change over time. Yet numerical models suffer from the intrinsic disadvantage of under-parameterization. The essential parameter set comprises apart from more kind of parameters compared to the analytical model also information about the spatial and temporal distribution of the parameters to consider site heterogeneity (Table 2). Yet knowledge about spatial and let alone temporal heterogeneities or statistical distributions of hydrogeological data is limited (Wachter & Dahmke, in press). Few studies on correlations between microbiological and hydrogeological heterogeneities indicate that subsurface microbiological properties have similar length scales, and the microbial properties appear to be spatially correlated to geologic, hydrologic and/or geochemical properties (Brockman & Murray 1997). As these data requirements are hardly fulfilled data gaps have to be compensated from literature or by deducing parameters from laboratory studies pointing out the difficulties of adapting and validating numerical models.

### Assessment of chlorinated solvent field studies

To assess applicability of MNA for chlorinated sites, data of field studies were compiled with the aim to deduce information on plume patterns and common investigation procedures at CAH sites. The results listed below are based on two database studies by McNab et al. (1999) and Aziz et al. (2000b), which aimed to deduce patterns of chlorinated solvent plumes:

- VC is unlikely to be the longest plume at a site, and should be less likely to reach downstream receptors than TCE and *cis*-DCE. It was detected at 58% of the sites (Aziz et al. 2000b).
- The plume at sites with BTEX were considerably shorter, their use as electron donors may explain the high incidence of reductive dechlorination (Aziz et al. 2000b; McNab et al. 1999).
- Chlorinated ethene plume lengths were moderately correlated with advection (Aziz et al. 2000b; McNab et al. 1999).
- Size of the source is considered to be the key factor impacting chlorinated solvent plume length (Aziz et al. 2000b; McNab et al. 1999).
- Effects of reductive dehalogenation on plume length are measureable, but only when influence of source area mass and groundwater velocity are factored out (McNab et al. 1999).
- TCE degradation rate constants increased with increasing temperature and H<sub>2</sub> concentrations (Aziz et al. 2000b).
- DNAPL were observed at 6 out of 24 sites (Aziz et al. 2000b).

Beyond these two database studies additional data were compiled from more recent publications to assess which kind of parameters are used to investigate CAH sites (Table 3). The results show that standard site investigations and assessment of NA efficiency are mainly based on hydrogeochemical parameters. Extensive field investigations including cost or time intensive microbiological or isotope measurements have been applied at only 2–7% of the sites. In general numbers of MNA field investigations are still small compared to the vast numbers of known sites contaminated with chlorinated ethenes. Therefore statistical ap-

proaches in terms of pattern identification which are based on compiled data sets and could be used for conceptual models at an early stage of site evaluation are up-to-date rather restricted (McGuire et al. 2003).

## Conclusions

In summary the criteria required to consider MNA in Germany are compared to available techniques to demonstrate and assess NA processes (Table 4). The results show that identification of source location and emission, though an important factor to determine plume lifetime and plume migration is strongly limited by missing investigation methods. This in turn complicates model prognoses on MNA duration. Nevertheless source information, though essential, should not be handled as a compulsory feature to accept

MNA and future research should address on this topic.

The requirements regarding plume inventory and dimension can be proven at least to some extent by available methods and techniques. However some of the criteria seem not reasonable i.e. no toxic intermediates and plume stability. Results from Aziz et al. (2000b) showed that VC was detected only at 58% of the sites, and is likely to be degraded under both anaerobic and aerobic conditions. Considering the large dimensions of CAH plumes efforts to demonstrate plume stability in the field might be disproportional as long as there is no receptor directly endangered. It is thus suggested to handle plume stability not as a compulsory criterion. Demonstration of reduction in contaminant load seems reasonable, however available investigation methods are insufficient (isotopes) or might negatively affect the NA potential of a site (IPT).

Table 4. Comparison of required criteria with available methods and parameters to demonstrate NA processes at a site

	Techniques available	Evaluation of techniques
<i>Source</i>		
Identification of position of DNAPL	Historical data, partitioning tracer tests	–
Small source inventory	Immission pump tests, direct-push	○
No dislocation in deeper aquifers	Drilling	–
Source removal (optional)	Hydraulic protection, physico-chemical mobilisation, ENA (biostimulation, bioaugmentation)	○
<i>Plume inventory and dimension</i>		
No toxic intermediates	Site investigation, measurement of VC concentrations	○
Plume stable or regressing	Site investigation, monitoring and compliance wells	○
No harm of further receptors	Site investigation, compliance well	○
Durable reduction of contaminant load, no dilution	Immission pump test	–
	Isotope measurements	–/○
	Modelling	○
<i>NA processes in the plume</i>		
Qualitative	Hydrogeochemical data	○/+
	Microbiological, isotope data	–/○
Quantitative evidence	Modelling	○/+
	Isotope data	–/○
Known degradation rates	Microcosm studies	○
	Field measurements	○
	modelling	○/+
Microbial activity	Microcosm studies, modelling	○
	Methods for direct evidence	–

Method evaluation is expressed by – = no/few, ○ = limited, and + = good significance and applicability.

Qualitative and quantitative evidence for efficiency of NA processes can be provided by combinations of the methods and parameters listed in Table 4. However main evidence is based on hydrogeochemical parameters and model approaches. Microbiological methods are restricted to prove the presence of bacteria. Isotope methods require cost-intensive investigation efforts and might fail in providing evidence for NA in case of fractionation factors being too small. Despite all these practical limitations MNA has been successfully demonstrated to be a potential and reliable remediation option for chlorinated sites. Current German guidelines thus should be modified to enable the feasible application of MNA as an alternative or additional remediation option.

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