The Effects of Contaminant Concentration on the Potential for Natural Attenuation

R&D Technical Report P2-228/TR

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Statement of Use
This technical report presents guidance on the assessment of potential natural attenuation processes of eighteen specific contaminants and in particular, the effects of contaminant concentration. It has been prepared for Agency staff who assess third party proposals for the use of monitored natural attenuation as part of a remedial strategy and for problem holders and their consultants who are considering or developing monitored natural attenuation schemes on a site-specific basis.

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The Environment Agency's Project Manager for R&D project P2-228 was Lamorna Zambellas, National Groundwater and Contaminated Land Centre. This project is part of the umbrella R&D project P2-169 "Strategic research project into the natural attenuation of pollutants in groundwater" which is managed by Dr Alwyn Hart, National Groundwater and Contaminated Land Centre. The project team also included Jonathan Smith, Theresa Kearney and Neil Foster.

EXECUTIVE SUMMARY

This document, which forms part of the Environment Agency's outputs relating to the use of monitored natural attenuation (MNA) as a potential remedial strategy for groundwater, addresses the following specific issues:

- the effects of contaminant concentration on the rate of natural attenuation (NA) processes in UK aquifer systems;

- the viability of extrapolation of degradation rate data from an overseas environment to UK conditions.

The project was based upon a literature review for 18 contaminants (phenol, benzene, toluene, ethylbenzene, xylenes, naphthalene, benzo(a)pyrene, methyl tert-butyl ether (MTBE), ethanol, Mecoprop, parathion, inorganic cyanide (CN^-), tetrachloroethene, trichloroethene, dichloroethene, vinyl chloride, 1,1,1-trichloroethane, dichloroethane) and five NA processes that are, in part, concentration dependent (diffusion, volatilisation, sorption, abiotic degradation and biodegradation).

UK aquifers were classified on the basis of the likely importance of these attenuation processes under prevailing conditions (fraction of organic carbon, flow mechanism, redox conditions and iron and manganese content).

A relatively small proportion of the available literature was found to contain clear information relating contaminant concentration directly to attenuation rate. Furthermore, there were very few data on attenuation processes in consolidated aquifers, particularly fractured sandstone and chalk systems.

Collation and interpretation of biodegradation data collected from the literature demonstrated that a range of contaminant concentrations exists within which biodegradation takes place at observable rates, albeit highly variable from site to site. Frequently, the limits of such ranges are defined by reported concentrations that can be considered to be the likely upper and lower bounds. At these elevated and very low concentrations, degradation occurs at much slower or negligible rates. The estimated threshold concentrations are listed for each contaminant in tabular form in this report.

Within the normal range for biodegradation, it was not possible to determine reproducible correlations between contaminant concentration and rate, despite the existence of a theoretical relationship between them. Furthermore, even between datasets from apparently relatively homogeneous aquifer types (e.g., low organic carbon alluvial sands), there were major variations in reported attenuation rates under similar conditions. Hence, rates reported in the literature for a specific contaminant and site (e.g., aerobic benzene degradation in a shallow, low organic carbon, sandy aquifer) can only be used as a guide to the likely degradation rate at another site with similar conditions. Derivation of estimates for the major consolidated aquifers in England and Wales was greatly hampered by the lack of published data.

Sorption processes may dominate contaminant fate and transport for certain contaminants (e.g., benzo(a)pyrene) or may have very little effect (e.g., phenol, ethanol, Mecoprop), regardless of concentration. However, for a 3rd group of contaminants (e.g., BTEX compounds, chlorinated solvents) sorption may have a significant impact on the migration rate, dependent upon environmental factors, particularly the fraction of organic carbon in the aquifer.

The following conclusions have been drawn with respect to sorption processes:

- Linear sorption can be adequate at low concentrations to quantify sorption;

- When considering a wide range of concentrations in heterogeneous sorption environments, nonlinear, Freundlich sorption behaviour, in which retardation magnitude varies with contaminant concentration, is likely to provide a better means of quantification. Variation in the magnitude of retardation at different concentrations can range from a factor of 2-3 up to, in one case, a factor of 20. At higher contaminant concentrations, less sorption than predicted by the linear model is likely although in some cases the linear model can provide a reasonable approximation over a range of concentrations;

- Other processes that could lead to errors of up to two orders of magnitude (typically these effects may lead to errors in retardation factors by a factor of 2 or 3) include:
    - cosolvency effects,
    - non-equilibrium sorption,
    - sorption to aquifer mineral content (if it has been assumed all sorption takes place within aquifer f_{oc})
    - nature and composition of aquifer f_{oc}.

In summary, contaminant concentration effects are important in the assessment of the viability of MNA as a remedial technology at a site. However, there appears to be no basis for prediction of a degradation rate based on concentration effects. Furthermore, translation of a degradation rate from one site to another appears to be impossible without introducing a broad range of plausible degradation rates for the site under investigation. These may vary seasonally, in different parts of the plume and for other site-specific reasons. Moreover, concentration effects are likely to be difficult to distinguish from other factors, in particular heterogeneity of hydrogeological and hydrogeochemical conditions of different sites, microbial communities, sampling and analytical variation and data interpretation.

For England and Wales, the uncertainty is compounded by the lack of a significant dataset on attenuation rates in aquifers. For these reasons, Environment Agency R&D Report 95 (Environment Agency, 2000a) emphasises the importance of "lines of evidence" for MNA established using site data gathered in the field over a reasonable period. Based on the literature review, site-specific rate data determined in the laboratory should be used with caution.

Keywords: MNA, sorption, biodegradation, aquifers, contaminant concentration.

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1. INTRODUCTION

Natural attenuation is the combination of physical, chemical, and biological processes in the subsurface that, under favourable conditions, act without human intervention or enhancement to reduce to acceptable levels the risk posed by contamination. Its application as a remedial option requires thorough and robust evaluation and monitoring, hence the use of the term *monitored natural attenuation* (MNA) to distinguish the technique from the underlying processes.

The approach to, and requirements for, the evaluation of MNA in groundwater in England and Wales has been documented in Environment Agency R&D Publication 95 (Environment Agency, 2000a). Clearly, MNA evaluation will need to be based on appropriate site-specific data. However, when properly applied, laboratory and field data from other sites may be a useful input to MNA evaluation, particularly in the early stages. Most published data that could potentially be used in this way has been generated in the laboratory or from field sites outside the UK. This does not negate the application of these data but expertise is required to interpret and extrapolate them. The same holds true for transposing data from the small number of reported UK field investigations of MNA to other sites.

A number of individual processes may contribute to the overall attenuation effect. In the majority of cases, it is the *degradative* processes that determine whether NA is protective of human health and the environment. Particularly important are biodegradation and, for a smaller number of compounds, chemical degradation processes. Since these, and other contributing processes such as sorption and volatilisation, are, in part, concentration-dependent, it is clear that an understanding of the relationship between contaminant concentration and the performance of individual natural attenuation processes is critical. *The objective of this project was to report on the effects of contaminant concentration on the potential for natural attenuation of dissolved contaminants in groundwater*.

2. APPROACH & RATIONALE

To ensure a practical end-product, the approach taken in this project was to assess:

- 18 compounds, selected as key representatives of important contaminant groups commonly detected in UK groundwater;
- processes occurring only for contaminants in solution.

Evaluation of each contaminant involved:

- Identification and collection of published literature and other available data on the effects of concentration on the rate of NA processes for representative contaminants common in UK aquifers.
- Collation and interpretation of these data to derive relevant relationships between process rates and contaminant concentration.
- Translation of these data for potential application for screening and validation of MNA (as described in Environment Agency, 2000a).
- Recommendation of necessary further research to fill knowledge-gaps.

The specific conclusions apply only to the compounds evaluated but the general approach and much of the background data could be applied for other contaminants.

2.1 Contaminant selection

The compounds evaluated in this project were selected as key representatives of major contaminant groups likely to be encountered in groundwater in the UK.

The contaminants evaluated are listed in Table 2.1. For information, their molecular structures are given in Appendix 4.

Potential interactions between contaminants were not specifically considered, except for certain defined combinations, namely:

- BTEX (benzene, toluene, ethylbenzene and xylene) components since these are frequently present dissolved in groundwater as a mixture arising from petroleum hydrocarbon contamination;
- BTEX and MTBE or ethanol, since these may be dissolved in groundwater as a mixture arising from unleaded petrol (gasoline) contamination;
- Chlorinated ethenes and ethanes, since some compounds may be generated from others during certain degradation processes that operate under certain environmental conditions.

In these specific cases, the implication of these interactions on natural attenuation performance is so great as to make their consideration mandatory in any MNA evaluation.

Table 2.1 Contaminants evaluated and their significance.

Contaminant group	Contaminants evaluated	Comments
BTEX	Benzene Toluene Ethylbenzene Xylenes	Potential origin as components of crude oil and petroleum products, coal tars, solvent wastes, etc. Usually present as mixtures. 3 isomers of xylene (*o*-; *m*- & *p*-) considered separately where there is a significant difference in their fates.
Polycyclic aromatic hydrocarbons (PAH's)	Naphthalene Benzo(a)pyrene	Components of coal tars, pitch, gasworks and coking plant wastes, etc. Minor component of crude oil and petroleum products. Relatively low solubilities, especially benzo(a)pyrene.
Fuel additives (oxygenates)	Methyl *tert*-butyl ether (MTBE) Ethanol	Evaluated only in the context of their use as oxygenates in unleaded petrol (gasoline).
Phenols	Phenol	Common component in coal tar, gasworks wastes, certain chemical processes, etc.
Pesticides	Mecoprop (2-(2-methyl-4-chlorophenoxy)propionic acid) Parathion (O,O-diethyl-O-*p*-nitrophenylphosphorothioate)	Representative types of pesticides commonly considered a threat to groundwater.
Chlorinated solvents	Tetrachloroethene (PCE) Trichloroethene (TCE) Dichloroethene (DCE) Vinyl chloride (VC) Trichloroethane (TCA) Dichloroethane (DCA)	Widely used as solvents (except VC; e.g. in degreasing, dry cleaning, chemical manufacture), used as intermediates in chemical manufacture. 3 isomers of DCE (1,1-; *cis*-1,2 & *trans*-1,2-) considered separately where there is a significant difference in their fates. 2 isomers of TCA (1,1,1- & 1,1,2-) considered separately where there is a significant difference in their fates 2 isomers of DCA (1,1- & 1,2-) considered separately where there is a significant difference in their fates Under certain conditions, conversion of more highly chlorinated compounds to lower chlorinated ones can occur.
Inorganic cyanide	Cyanide salts (as CN^-)	Cyanide may be encountered as various metal-cyanide complexes and free cyanides, for example at metal-plating and gasworks sites.

2.2 UK aquifer classification

Two issues face those attempting to assess the effects of contaminant concentration on the potential for natural attenuation in the UK:

- aquifers in the UK are hydraulically complex and heterogeneous bodies of rock that exhibit significant variability at different scales of interest (Allen *et al.*, 1997). As most NA processes are in part dependent on the nature of the aquifer, this means that using generalised classifications of UK aquifers needs to be complemented by an understanding of likely site specific variability at the scale of interest;

- most NA data collated by this project from the literature refer to either laboratory or overseas environments which need to be translated to UK environments if they are to be of practical use in assessing UK sites.

In order to address these issues, the following methodology has been adopted:

- the main types of aquifers and aquitards in the UK have been classified on the basis of flow mechanism, fraction of organic carbon, potential redox conditions, biological activity and, where possible, iron and manganese content;

- collated degradation rate data were assessed in terms of their applicability to UK environments;

- it was hoped that a conversion factor would be applied by assessing differences in degradation rates between UK and overseas conditions and differences in degradation rates between laboratory and field conditions. However, the quality of the data in the literature was sufficient to make generic statements only.

It is important, however, that where degradation rates are being estimated for sites in the UK, that consideration is given to the effect of groundwater temperature. UK groundwater is typcially 10^{o}C. Groundwater in warmer climates (e.g. Florida, California) may be significantly warmer (often 15-22 ^{o}C) and more rapid biochemical processes might be expected to occur.

Table 2.2 presents a classification of selected UK aquifer types while Table 2.3 presents classification of locally major aquifers, minor aquifers and non-aquifers.

TABLE 2.2 : CLASSIFICATION OF MAJOR UK AQUIFERS

	Flow Mechanism (local variations may occur and be listed in regional EA appendices):			**Fraction of organic carbon – foc all figures expressed as a percentage:**			**Redox Conditions:[3]**		**Formation Fe Content**	**Formation Mn Content**
Aquifer:	Fracture	Combined	Intergranular	(<0.1%)	(0.1-1.0%)	(>1.0%)	Oxidising, oxidised or aerobic (generally unconfined)	Reducing, reduced or anaerobic (generally confined)		Descriptive
Upper and Middle Chalk		✔		✔ (Mean range 0.027 – 0.036)[1]			✔	✔	Very low	Mn nodules are known to exist along fracture surfaces.
Lower Chalk		✔		✔ (Mean 0.045)[1]	(✔ increases with depth to a max of 0.12)[1]		✔	✔	Very low	Mn nodules are known to exist along fracture surfaces.
Lower Greensand			✔	✔ (Mean 0.04 in top 65m)[2]	(✔ up to 0.19 in lower 20m)[2]		✔	✔	No data, likely to be locally high	No data, likely to be moderate
Jurassic Limestones: Great Oolite Group	✔			✔ (little data: likely to be low)			✔	✔	No data	No data
Jurassic Limestones: Lincolnshire Limestone	✔			✔ (min 0.01)[1]	✔ (mean range 0.12-0.31 depending on redox state of rock)[1]	(✔ max values of 1.5-2.7)[1]	✔	✔	No data	No data
Permo-Triassic Sandstones		✔		✔ (mean 0.028)[1] 0.048, Four Ashes	(✔ max 0.15 Nottingham Area)[4]		✔	✔	Variable, 0.0057%[5] , 0.55%[4]	0.0066%[5] , 0.005%[4]
Magnesian Limestone	✔			✔ (little data: estimated content low)			✔	✔	No data	No data
Carboniferous Limestone	✔			✔ (little data : estimated content low)			✔	✔	No data	No data

1 : Data from Steventon-Barnes, unpublished PhD thesis, University College London, 2000
2 : Data from McLeod (1998)
3 : Both classifications are indicated where differing conditions generally occur in different regions of the formation in the UK
4 : Data from Thornton *et al.* (2000)
5 : Unpublished data, median values of 108 samples (Gooddy, 2001)

TABLE 2.3 OTHER UK ENVIRONMENTS (e.g., local major aquifers, minor aquifers, non-aquifers for which data were available)

	Flow Mechanism (local variations may occur and be listed in regional EA appendices):			Fraction of organic carbon – foc all figures expressed as a percentage:			Redox Conditions[3]		Solid Fe Content	Solid Mn Content
Aquifer/ Formation:	Fracture	Combined	Intergranular	(<0.1%)	(0.1-1.0%)	(>1.0%)	Oxidising, oxidised or aerobic (generally unconfined)	Reducing, reduced or anaerobic (generally confined)		
Alluvium : Unconsolidated silts and clays (locally a minor aquifer)			✔	✔(min 0.06)[1]	✔(mean 0.74)[1]	✔(max 6.2)[1]	✔	✔	Likely to be variable	Likely to be low
Fluvio-Glacial Sand & Gravel (locally minor or major aquifer)			✔	✔(min 0.02)[1]	✔(mean 0.17)[1]	✔(max 1.2)[1]	✔		Likely to be low	Likely to be low
Devonian Old Red Sandstone		✔		No data	No data	No data	✔	✔	Likely to be moderate to high	No data
Carboniferous Coal Measures (locally a minor aquifer)		✔			✔(0.2)[9]	✔(mean 2.2[5], range of 2.8-11.3[6])	✔	✔	Likely to be moderate to high	Likely to be moderate to high
Mercia Mudstone Group		✔		✔(variable, assumed range)	✔(variable, assumed range)		✔	✔	Likely to be high	No data
Jurassic aquitards e.g. Lias, Kimmeridge Clay, Oxford Clay			✔			✔(mean range of 4.8-5.1[7,8])		✔	No data	No data
Marl within Lincolnshire limestone			✔		✔(mean 0.44)[1]	✔(max of 1.5)[1]	✔	✔	No data	No data
Glacial Till		✔(very variable)		✔(min 0.03)[1]	✔(mean 0.28)[1]	✔(max of 1.0)[1]	✔	✔	Likely to be moderate to high	No data
Made Ground			✔	Likely to be extremely variable and site specific	Likely to be extremely variable and site specific	Likely to be extremely variable and site specific	✔	✔(often reducing because of chemical components of made ground)	No data	No data

1 : Data from Steventon-Barnes, unpublished PhD thesis, University College London, 2000
2 : Data from McLeod (1998)
3 : Both classifications are indicated where differing conditions generally occur in different regions in the UK
4 : Data from Thornton *et al.* (2000)
5 : Data from BGS (1971)
6 : Data from Dobson and Kinghorn (1987)
7 : Data from Kenig *et al.* (1994)
8 : Data from Norry *et al.* (1994)
9 : Data from Mouvet *et al.*, Bourg *et al.* (1993)

3. CONCENTRATION-DEPENDENT NATURAL ATTENUATION PROCESSES

3.1 Diffusion

Molecular diffusion describes the process by which chemicals in solution or gas phase migrate along their concentration gradients. Diffusion represents the tendency for migration from areas of high concentration to areas of low concentration.

The process of molecular diffusion is described by Fick's laws, which can be applied to a steady state system where there is a constant concentration gradient or a transient case where the concentration gradient changes with time.

Diffusion in contaminant transport assessment is typically accounted for by combining the effects of mechanical dispersion (i.e. dispersion due to migration along differing flow paths) and molecular diffusion, into a single hydrodynamic dispersion parameter.

The processes of sorption, biodegradation and diffusion can become interdependent when rate-limited or non-equilibrium sorption-desorption (which are essentially diffusion processes) cause biodegradation rates to be limited.

3.2 Volatilisation

Partitioning of a contaminant between the liquid phase and the gaseous phase is governed by Henry's Law (for volatilisation from dissolved phase) and vapour pressure (for volatilisation from free phase).

The Henry's law constant (H) for a contaminant is the ratio of the equilibrium concentration of the contaminant in air to the concentration dissolved in water under defined conditions. Values of H vary over several orders of magnitude for the compounds discussed in this project.

If the concentration of a contaminant in groundwater increases, the concentration of that contaminant in the vapour phase above the water table will also increase in proportion to (i) the vapour pressure of the contaminant and (ii) the magnitude of the increase of its concentration in the groundwater. However, it has been shown by Chiang *et al.* (1989), that less than 5% of the mass of dissolved BTEX is lost to volatilisation from the groundwater in the saturated zone. Furthermore, Rivett (1995) reported that very low or negligible chlorinated solvent concentrations will be detectable in soil gas for contaminants present in a plume more than 1 metre below the water table due to downward groundwater velocity near the water table.

3.3 Sorption

3.3.1 Introduction

Sorption describes the processes by which a contaminant migrating through porous media partitions between the solid and aqueous phases. The effect of sorption is to slow or retard the rate of migration of the contaminant relative to the average (advective) groundwater flow velocity. Groundwater contaminant plumes comprising a number of contaminants may exhibit a "chromatographic" separation along the groundwater flow path due to variations in the sorptive properties of the constituent contaminants.

Sorption can be determined experimentally by either batch or column testing. Brief descriptions of these tests can be found in Appendix 2.

Sorption can be a reversible, irreversible or hysteretic reaction. In any case, sorption does not result in a permanent mass reduction although desorption rates are often very slow in comparison and so mass loss may be considered permanent in the timeframe of interest.

In the case of a reversible reaction, it should be noted that at a given contaminant concentration some portion of the contaminant is partitioning to the aquifer matrix and some portion is also desorbing and re-entering solution as in an equilibrium reaction. As contaminant concentrations change, the relative amounts of contaminant that are sorbing and desorbing will simultaneously change. For example, as dissolved contaminant concentrations decrease (perhaps due to plume migration or contaminant biodegradation and dilution), the amount of contaminant re-entering solution will likely increase. If the rate of these reactions is fast relative to the groundwater flow velocity, then equilibrium sorption is assumed.

3.3.2 Causes of sorption

Sorption of dissolved contaminants can occur as a result of:

- electrostatic forces leading to cation exchange - the replacement of a sorbed ion by the contaminant;
- the action of van der Waals forces, hydrogen bonding, ligand exchange, dipole forces and hydropbobic forces which cause adsorption, attachment of a contaminant to a solid surface;
- covalent bonding between contaminant and aquifer matrix, named chemisorption;
- diffusion of a contaminant into the structure of a porous particle, named absorption.

For practical purposes, these processes are often grouped and assessed as a single sorption parameter. In this report the term sorption is used to cover partitioning processes in general (that is, partitioning between solute and solid, not NAPL or vapour phase) and the process of attachment to the aquifer matrix (retardation) in particular. Where necessary, sorption will be discussed in terms of actual mechanisms (adsorption, absorption, etc). The process of contaminants re-entering solution is referred to as desorption.

3.3.3 Sorption Models, Isotherms & Retardation Factors

Three equilibrium sorption models are generally used to describe sorption of contaminants. Two of these (Langmuir and Feundlich) describe different types of non-linear sorption behaviour while the third, linear sorption, is a special case of Freundlich sorption where the slope of the isotherm is a constant. Characteristic adsorption isotherm shapes are illustrated by Figure 3.1 while detailed descriptions of the models and retardation factors are found in Appendix 2.

Allen-King *et al.* (1996) noted that both Freundlich and Langmuir isotherms are essentially linear when concentrations are low, as may be the case in a dilute contaminant plume. However, near NAPL sources, dissolved concentrations may be sufficiently high that isotherm nonlinearity may be important see section 4 and Rivett *et al.,* 2001).

3.3.4 Sorption of organic, hydrophobic contaminants

In general the partition coefficient (K_d) is controlled by the degree of polarity (low polarity is a characteristic of hydrophobic molecules) of the contaminant and the total surface area of the aquifer matrix. Due to the high surface area to volume ratios of organic carbon and clay minerals in the solid matrix, surface polarity and chemistry, these components tend to be the key geological controls on the degree of sorption of a particular contaminant.

A discussion of the sorption of organic, hydrophobic contaminants and the role of K_d, K_{oc}, K_{ow} and f_{oc} (both quantity and nature of the organic carbon) can be found in Appendix 2.

Table 3.1 summarises K_{ow}, K_{oc}, K_d and solubility data for the contaminants of interest in this project. The trends described above are clearly visible in this table (see also section 4.3).

Table 3.1: Sorption parameters for a theoretical environment with uniform and constant organic carbon content

Contaminant:	K_{ow} (l kg^{-1}) (all Ref A)	K_{oc} (l kg^{-1})	K_{oc} data	Theoretical K_d (l kg^{-1})*	Theoretical Retardation Factor**		Contaminant velocity as a result of sorption effects (% of advective velocity assuming sorption is the only attenuation process acting)	Solubility (mg l^{-1}) (@25°C) (all Ref A)	Molecular Weight	10^{-5} M (mg l^{-1}) : aqueous phase contaminant concentration above which sorption isotherms depart from linearity (Karickhoff, 1979)
Benzo(a)pyrene	933,254	916,000	H	720.00	5,761.00		0.02	0.002	252	2.52***
Naphthalene	1,995	1,122	C	1.68	14.46	Highly sorbed	7	31	128	1.28
Parathion	6,760	500	F	0.8	7.00		14.3	6.5	291.3	2.91
Ethylbenzene	1,412	468	C	0.70	6.62		15	169	106	1.06
o-xylene	1,318	422	E	0.63	6.06		16	178	106	1.06
m-xylene	1,584	405	E	0.61	5.86		17	161	106	1.06
Tetrachloroethene (PCE)	363[B]	224	D	0.34	3.69		27	200	165.8	1.66
Toluene	537	190	E	0.29	3.28		30	526	92	0.92
1,1,1 trichloroethane (TCA)	309	183	D	0.27	3.20		31	1,500	133	1.33
Trichloroethene (TCE)	263	119	D	0.18	2.43		41	1,100	131.5	1.32
1,2 dichloroethane (DCA)	30	93	D	0.14	2.12		47	8,520 (@20°C)	99	0.99
Benzene	135	79	C	0.12	1.95	INCREASING SORPTION	51	1,780	78	0.78
cis-dichloroethene (DCE)	72	49	D	0.07	1.59		63	3,500	97	0.97
1,1 dichloroethane (DCA)	62	40	D	0.06	1.48		68	5,060	99	0.99
trans-dichloroethene (DCE)	123	36	D	0.05	1.43		70	6,300	97	0.97
Vinyl chloride (VC)	42	28	D	0.04	1.34		75	8,800	62.5	0.63
Phenol	25	27	C	0.04	1.32		76	82,800	94	0.94
Mecoprop	18 (ref I)	12.9	G	0.02	1.16	Insignificant sorption	86	620 (@ 20°C)	214.5	2.14
MTBE	8.7	6.1	G	0.01	1.08		93	51,000	88.15	0.88
Ethanol	0.48	0.31	G	0.0005	1.004		99.6	1,000,000	46	0.46

General assumptions of this table are sorption to mineral fraction is ignored, f_{oc} composition is uniform, sorption reactions are in equilibrium and sorption is linear. All of these issues are discussed further in the text.

* assumes f_{oc} = 0.0015 (0.15%) ** assumes aquifer bulk density = 1.6 g cm^{-3}, porosity = 0.2 and f_{oc} = 0.0015 (0.15%) *** In the case of benzo(a)pyrene, one half of the aqueous solubility is the relevant threshold value as it is lower than 10^{-5}M (Karickhoff, 1979)

Data selected arbitrarily from published sources listed below

A = Howard & Meylan, 1997

B = Montgomery, 1996

C = Fetter, 1998 and/or 1999

D = Howard 1989 and/or Howard 1990 as quoted in US EPA Technical Protocol, 1998. Mean or median of range is given where multiple values exist

E = Mean, recommended value from various sources as quoted in US EPA Technical Protocol, 1998

F = Davidson *et al.* 1980

G = calculated from k_{ow} data using method of Rao & Davidson (1980) as quoted in Fetter (1999)

H = USEPA 1994

I = Agrochemicals Handbook, 3rd Edition, 1994, Royal Society of Chemistry

3.3.5 Non-equilibrium (kinetic) Sorption

A further set of sorption models can be used to describe the process of non-equilibrium sorption in which the rate of change of concentration due to sorption is limited by the sorption processes thus preventing equilibrium being reached. In this case the sorption processes of absorption and diffusion are at work. Two specific mechanisms act to transport contaminants:

- migration of contaminants into or out of the internal structure of the organic matter (controlled by the chemical structure of the organic matter or steric control);

- migration of contaminants into or out of the internal structure of the aquifer particles (intra particle diffusion).

These diffusion processes typically occur at slower rates than surface adsorption and are governed by Fick's Laws. Moreover, these processes act for slower hydrophobic sorption of organics into the structure of the aquifer matrix f_{oc} rather than faster surface-based adsorption to clay minerals (which is generally important for low f_{oc}-low K_{ow}-high clay content systems).

Non-equilibrium sorption models are described in the literature (e.g. Fetter, 1999) and have been applied to contaminant transport problems. These processes, which can be concentration dependent, have important implications for:

- the length of time over which sorption experiments should take place;
- the estimation of sorption parameters in low permeability environments (i.e. retardation factors often increase over longer timescales due to the effect of non-equilibrium sorption processes);
- the estimation of desorption parameters which can take place over longer time scales;
- bioavailability of contaminants at low concentrations;
- degree of attainment of sorption predicted by equilibrium distribution coefficients;
- attainment of equilibrium sorption under high flow rates.

3.3.6 The significance of sorption to MNA

Sorption can have three distinct implications for NA processes:

- Removal of contaminant mass from a groundwater plume and/or removal of contaminant mass from infiltrating waters in the unsaturated zone. This reduces the overall mass in the plume and has the *effect* of decreasing the velocity of the contaminant plume. The mass removed remains sorbed to the solid material in the aquifer until such time as desorption can occur due to reversed concentration gradients (i.e. higher concentrations in the sorbed phase than the dissolved phase) at longer time intervals. Desorption rates are typically diffusion-controlled and occur at slow rates which may mean they can be ignored due to the higher relative importance of other processes such as biodegradation. However, desorption also has the potential to continue adding the contaminant to groundwater long after other sources are removed;

- Increase of contaminant travel time to a receptor due to retardation processes will give specific processes (such as radioactive decay) more time to act upon contaminants relative to advective transport;

- The concept of 'bioaccessibility'. The biodegradation of groundwater contaminants normally requires them to be dissolved in aqueous solution; therefore, adsorption and absorption may render contaminants unavailable for biodegradation unless and until desorption into the aqueous phase takes place

The effect of "bioaccessibility" on contaminant biodegradation rate is particularly significant for highly insoluble, hydrophobic contaminants (such as benzo(a)pyrene) but is also important for all other contaminants when they are present at extremely low concentrations. This is discussed further in Section 4.3, below.

A summary of the key controlling factors for sorption processes is presented below:

Table 3.2 Key controlling sorption parameters

Parameter	**Controlling factors**
K_d – distribution coefficient	• properties of contaminant molecules - especially hydrophobicity or degree of polarity (described by K_{oc} and K_{ow}); • f_{oc}; • composition of f_{oc}; • mineral (clay) content for low f_{oc}/low K_{ow} systems.
K_{oc} – organic carbon distribution coefficient	• degree of hydrophobicity of contaminant; • composition of f_{oc}.
K_{ow} – octanol-water distribution coefficient	• degree of hydrophobicity of contaminant.
f_{oc} – fraction of organic carbon content f_{oc} composition Mineral content or clay content	• geological depositional environment; • post-depositional history.

3.4 Chemical (abiotic) degradation

This term is used to describe the transformation of a chemical into simpler compounds without the involvement of a biological component. The most important chemical degradation reactions of organic contaminants in aquifers are:

- Hydrolysis
- Oxidation-reduction (redox)
- Elimination

The kinetics of chemical degradation reactions data applicable to MNA evaluation are generally based on the use of zero-order and first-order kinetics. The basis of these estimations and the effect of temperature on rate is given in Appendix 3.

The rates of chemical degradation reactions in aquifers are generally slower than biologically mediated reactions and reaction half-lives (see Appendix 3) are usually measured in years.

3.5 Biodegradation

Many organic contaminants (and certain inorganic contaminants such as cyanide and nitrate) can be biodegraded in aquifers by naturally occurring microorganisms.

For some compounds and under certain conditions, intermediate organic biodegradation products may be produced, which may be more or less persistent than the parent compound and more or less hazardous. Such potential intermediate product generation needs to be considered as part of the risk assessment for the site. Information on specific pathways and conditions where such intermediates may arise is given for individual compounds in Section 4.1.

There is a very large literature on biodegradation and it is not necessary to understand in detail the processes involved or the organisms responsible. Those interested should consult one or more of the many reviews on this subject, (e.g., Ratledge, 1994; Gibson, 1984; Hardman, 1991; Heider *et al.*, 1998; Lee *et al.*, 1998; Azadpour-Keeley *et al*., 1999; National Academy of Sciences Committee on Intrinsic Bioremediation, 2000). However, it is necessary to understand the basic types of biodegradation processes and that the rates and extent of biodegradation are dependent on contaminant concentration and other environmental factors.

3.5.1 Biodegradation processes

The microorganisms involved in the biodegradation of organic contaminants discussed in this report, oxidise organic substrates (“electron donors”) as a source of carbon and energy, while utilising a respiratory substrate (the “terminal electron acceptor”). Many microorganisms can utilise oxygen as the respiratory substrate (“aerobic” metabolism). Other microorganisms can metabolise in the absence of oxygen and utilise one or more alternative respiratory substrates (“anaerobic” metabolism; Table 3.3).

The presence of large amounts of natural organic matter or organic contaminants in groundwater will tend to lead to a rapid biological consumption of dissolved oxygen in the groundwater. Under such conditions anaerobic conditions will predominate, unless the rate of recharge is sufficient to supply adequate oxygen.

Table 3.3. Major respiratory substrates and processes. The typical geochemical markers that can be measured in groundwater as indicators of the microbial processes are indicative values only – there may be significant overlap of redox zones and processes in the field.

Process	Basic respiratory reaction	Typical geochemical markers
Aerobic	$O_2 \rightarrow H_2O$	Significant dissolved oxygen (>0.5 mg l^{-1}) Depletion of dissolved oxygen associated with biodegradation Redox potential >+200 mV
Denitrification	$NO_3^- \rightarrow N_2$	Low dissolved oxygen (<1 mg l^{-1}) Redox potential 0 to +250 mV Depletion of NO_3^-
Manganese-reduction	Mn (IV) (insoluble) → Mn (II) (dissolved)	Low dissolved oxygen (<0.1 mg l^{-1}) Redox potential –100 to +100 mV Increase in dissolved Mn
Iron-reduction	Fe (III) (insoluble) → Fe (II) (dissolved)	Low dissolved oxygen (<0.1 mg l^{-1}) Redox potential –100 to +100 mV Increase in dissolved Fe
Sulphate-reduction	$SO_4^{2-} \rightarrow S^{2-}$	No dissolved oxygen Redox potential typically <-200 mV Depletion of SO_4^{2-} Increase in H_2S, S^{2-}
Methanogenesis	Certain organic compounds → CO_2 + $H_2 \rightarrow CH_4$	No dissolved oxygen Redox potential typically <-450 mV Increase in CH_4

The biodegradation processes that operate under aerobic and anaerobic conditions are often very different in rate and end-product; indeed, many contaminants can only be biodegraded under specific conditions. Therefore, an understanding of the processes operating at different points in the contaminant plume is critical in evaluating MNA and performing a thorough risk assessment.

Aerobic biodegradation

In the presence of oxygen, many organic contaminants can be directly utilised as carbon and energy sources by microorganisms. However, certain compounds are resistant to significant biodegradation under aerobic conditions; important examples are many of the more highly chlorinated aliphatic and aromatic compounds, such as tetrachloroethene, trichloroethene and hexachlorobenzene.

As well as direct utilisation, certain organic contaminants can be subject to degradation by "co-metabolism" (fortuitous degradation). The compounds that can support co-metabolism are specific to the contaminant; an example is the co-metabolic biodegradation of trichloroethene by microorganisms utilising certain carbon and energy sources (e.g., methane, propane, butane). Co-metabolism under aerobic conditions can provide a mechanism by which certain compounds are degraded that may otherwise persist when oxygen is present. However, the simultaneous presence of aerobic conditions, the growth substrate, and contaminant under suitable conditions for co-metabolism is likely to be rare in a plume, except in highly localised zones (National Academy of Sciences Committee on Intrinsic Bioremediation, 2000). Therefore, aerobic co-metabolism will not be considered further in this report.

Anaerobic biodegradation

Anaerobic biodegradation can involve the direct utilisation of contaminants as a carbon and energy source. Certain organic compounds, particularly chlorinated solvents (e.g., tetrachloroethene, trichloroethene) and aromatics (e.g., pentachlorophenol), can also be biodegraded by other mechanisms under anaerobic conditions. Both processes are associated with highly-reducing conditions (redox potential below -150 mV) and require the presence of a source of carbon and energy, either other biodegradable organic contaminants or natural organic matter

Reductive dechlorination and dehalorespiration both of these processes involve the stepwise removal of chlorine atoms from chlorinated contaminants and their replacement by hydrogen. For example, tetrachloroethene will be degraded through trichloroethene, *cis*-1,2-dichloroethene and vinyl chloride to ethene.

Reductive dechlorination is a co-metabolic process, whereas dehalorespiration is the utilisation of chlorinated compounds as a respiratory substrate. So far, dehalorespiration has been demonstrated to occur for chlorinated ethenes and certain chlorinated aromatics (El Fantroussi *et al.*, 1998).

3.5.2 Biodegradation kinetics

Reported biodegradation rate data applicable to MNA evaluation are generally based on the use of one of three expressions for estimation, namely Monod, zero-order and first-order kinetics (Suarez & Rifai, 1999). The basis of these methods is given in Appendix 3.

There has been debate over the significance of estimates made by these different methods in respect of the relevance of the derived rates to the field. *The authors of this report believe that the inaccuracies arising from using an inappropriate kinetic model to derive biodegradation rates are insignificant compared to the uncertainties arising from sampling design, sample collection and processing, subsurface heterogeneity and the estimation of groundwater flow properties. Furthermore, it is likely that different kinetic models may be appropriate for different zones of a plume*. Hence, it is concluded that a detailed evaluation of biodegradation kinetic models is unnecessary for screening MNA performance.

Suarez & Rifai (1999) noted that small changes in biodegradation rate and groundwater velocity could have a major impact on plume behaviour predictions made by many of the common groundwater data and transport models. *In view of the uncertainty inherent in determining field values for these parameters, it is clearly necessary for sensitivity analysis to be included in the modelling programme used in the MNA evaluation*.

3.5.3 Impact of concentration on biodegradation

Contaminant concentration can have two distinct effects on biodegradation, as illustrated schematically in Figure 3.2.

At very low concentrations, the bioavailability of the contaminants to the degradative organisms may become reduced to the extent that biodegradation may cease. This may be associated with degradative microorganisms being inactive when their carbon and energy source is present only at extremely low concentrations ("oligotrophic" conditions). It is clear from both theoretical and experimental studies of microbial metabolism that there exist concentrations of contaminants below which metabolism of the compound is not induced (S_{ind}) or cannot continue (S_{min}). S_{ind} can be viewed as the minimum concentration necessary for the induction of biodegradative enzymes, whereas S_{min} is the lowest substrate concentration at which the microorganisms gain more energy from the consumption of a compound than they have to expend to metabolise it. (Boethling & Alexander, 1979).

Adsorption and absorption processes may remove the contaminant from the aqueous phase and thereby significantly reduce the rate of biodegradation. This may be particularly significant for highly insoluble, hydrophobic contaminants (e.g., benzo(a)pyrene). For example, Bosma *et al.* (1997) studied the effect of bioavailability on the biodegradation potential of the hydrophobic contaminant α-hexachlorocyclohexane under carefully controlled conditions in the laboratory. They found that the rate of biodegradation was totally dependent on the mass transfer of contaminant from the sorbed to the dissolved phase and that intrinsic microbial activity limited degradation rate only in rare cases.

This phenomenon has been observed experimentally for contaminants and naturally occurring organic compounds (Morgan & Dow, 1986). S_{ind} values have not been commonly measured; laboratory studies suggest that are generally in the order of a few $\mu g\, l^{-1}$ (Boethling & Alexander, 1979; Spain & van Veld, 1983). Data on S_{min} are even more difficult to come by because S_{min} is frequently below the analytical detection limit for the individual compound. Where data do exist, they have been measured under laboratory conditions and are included for specific contaminants in Section 4.2.

At high concentrations, there may be direct contaminant toxicity to the biodegradative microorganisms, which may reduce the rate of biodegradation and ultimately prevent it entirely. A similar toxicity effect may result when strictly anaerobic organisms are exposed to oxygen. Such events do not necessarily mean that the biodegradative microorganisms have been killed; microorganisms may enter a dormant state or persist within biofilms or sheltered niches within the aquifer and become active when conditions return to tolerable levels. The thresholds at which inhibition may become evident is dependent on both the chemical and the tolerance of the microbial population present. These will be discussed for the individual contaminants in Section 4.

4. RESULTS AND INTERPRETATION

This section of the report reviews the identified literature on a contaminant group basis for degradative mechanisms (Section 4.1) and sorption (Section 4.3) with a particular emphasis on the effects of contaminant concentration. Section 4.2 presents our interpretation of the degradative rate data against UK conditions.

4.1 Degradative attenuation mechanisms

4.1.1 Benzene, toluene, ethylbenzene and xylenes (BTEX)

The natural attenuation of BTEX components dissolved in groundwater is widely recognised as a common phenomenon. For example, in a recent survey of over 600 plumes in the USA (Newell & Connor, 1998), natural attenuation was significant in the great majority of cases and biodegradation was by far the most important attenuation process.

Therefore, the most critical question with BTEX natural attenuation is whether the appropriate biodegradative microorganisms are active under the intrinsic conditions and can biodegrade the contaminants at a rate that is protective of the receptors. This may be constrained for the individual components by contaminant concentration, *in situ* conditions and interactions between the components.

Benzene

There are no significant abiotic degradation pathways for benzene in groundwater.

Benzene is readily biodegradable under aerobic conditions at appropriate concentrations (National Academy of Sciences Committee on Intrinsic Bioremediation, 2000; Suarez & Rifai, 1999). Benzene can also be biodegraded under anaerobic conditions including denitrifying, iron-reducing, sulphate-reducing and methanogenic conditions (e.g., Borden *et al.*, 1997; Morgan *et al.*, 1993; Gieg *et al.*, 1999; Nales *et al.*, 1999; Kazumi *et al.*, 1997; Edwards & Grbic - Galic 1992; Anderson & Lovley, 1999). However, the performance of anaerobic benzene biodegradation is highly site specific –a significant proportion display no significant anaerobic benzene biodegradation. The reasons for this difference between sites are not well understood.

In a detailed survey of groundwater biodegradation rates, Suarez & Rifai (1999) compiled data from a number of published field and laboratory investigations of aerobic and anaerobic benzene biodegradation. These results are summarised in Figures 4.1 and 4.2. Although, the individual datapoints are not individually presented in Suraez & Rifai (1999), the derived ranges provide a useful benchmark that has been used in the derivation of UK rates in this project. No information on the effects of contaminant concentration on biodegradation rate were reported.

A similar survey of anaerobic biodegradation rates by Aronson & Howard (1997) concluded that “this review of anaerobic benzene biodegradation rates provides a relatively complex and conflicting picture” and that “anaerobic benzene biodegradation appears to be more site specific than is true for the other monoaromatic hydrocarbons”. They therefore suggested a wide range of rate constants to be applied in groundwater fate and transport models for anaerobic benzene plumes, namely zero (no anaerobic biodegradation) to 0.0033 day^{-1} (half-life of 210 days), which was the mean value of the entire field and laboratory data set that they

considered. No attempt was made by those authors to correlate rate with starting contaminant concentration; analysis of their dataset was made for this project but no clear correlation between concentration and rate could be discerned (Figure 4.3).

Inhibition of biodegradation by elevated concentrations of benzene is well-documented. Unpublished Cases 1 and 2 summarised in Appendix 8 of this report suggest that inhibition may occur at 50 mg l^{-1}, although Case 3 and some published reports (e.g., Thierrin *et al.*, 1993) suggest that significant biodegradation can take place at groundwater concentrations up to 100 mg l^{-1}.

Some attempts have been made to measure S_{min} for benzene (the minimum substrate concentration at which biodegradation can be sustained). In laboratory experiments this has variously been reported to be in the range <1 μg l^{-1} to 5 μg l^{-1} (Kuhlheimer & Sunderland, 1985; Jensen *et al.*, 1985). Field data (Barker *et al.*, 1987) suggest that biodegradation to below 1 μg l^{-1} is perfectly feasible.

Toluene

There are no significant abiotic degradation pathways for toluene in groundwater.

Toluene is generally considered the most readily biodegradable of the BTEX components under aerobic and anaerobic conditions (e.g., Borden *et al.*, 1997; Morgan *et al.*, 1993; Gieg *et al.*, 1999; Anderson & Lovley, 1999; Kirtland *et al.*, 2000; Beller *et al.*, 1992) and it is rare for no biodegradation to take place.

In a detailed survey of groundwater biodegradation rates, Suarez & Rifai (1999) compiled data from a number of published field and laboratory investigations of aerobic and anaerobic toluene biodegradation. These results are summarised in Figures 4.1 and 4.2. Although, the individual datapoints are not individually presented in Suraez & Rifai (1999), the derived ranges provide a useful benchmark that has been used in the derivation of UK rates in this project

A similar survey of anaerobic biodegradation rates by Aronson & Howard (1997) reported mean first-order rate constant values from laboratory and field studies under denitrifying, iron-reducing, sulphate-reducing and methanogenic conditions to be 0.63 day^{-1}, 0.021 day^{-1}, 0.049 day^{-1}, and 0.029 day^{-1}, respectively. They suggested a range of rate constants to be applied in groundwater fate and transport models for anaerobic toluene plumes, namely 0.00099 day^{-1} (half-life of 700 days), which was the lowest measured field value, to 0.059 day^{-1} (half-life of 12 days), which was the mean value of the entire field and laboratory data set that they considered. No attempt was made by those authors to correlate rate with starting contaminant concentration; analysis of their dataset was made for this project but no clear correlation between concentration and rate could be discerned (Figure 4.4).

Toluene is of relatively low toxicity to microorganisms. Indeed, a number of laboratory studies have demonstrated biodegradation in the presence of free-phase toluene (e.g., Collins & Daugulis, 1999a, b; Paje *et al.*, 1997). However, inhibitory thresholds in the field are difficult to specify, especially where toluene is present with other BTEX components, as is almost always the case. Data from Davis & Madsen (1996) suggest that toluene alone at concentrations up to *circa* 200 mg l^{-1} are unlikely to have a significant inhibitory effect on biodegradation.

Ethylbenzene

There are no significant abiotic degradation pathways for ethylbenzene in groundwater.

Ethylbenzene is normally readily biodegraded under aerobic conditions (National Academy of Sciences Committee on Intrinsic Bioremediation, 2000; Suarez & Rifai, 1999). Ethylbenzene can also be biodegraded under anaerobic conditions (e.g., Barbaro & Barker, 2000; Rabus & Heider, 1998; Thierrin *et al.*, 1993) but performance is highly site specific.

No evidence was found of a clear correlation between aerobic ethylbenzene concentration and biodegradation rate under field-relevant conditions. Suarez & Rifai (1999) reviewed over 80 reported cases of ethylbenzene biodegradation but found insufficient data to permit the derivation of mean biodegradation rates for this compound. This apparently reflected the fact that ethylbenzene was not commonly distinguished from other BTEX components in such studies. The mean value of the few individual datasets for aerobic ethylbenzene biodegradation gave a mean zero-order rate constant of 0.29 mg l^{-1} day^{-1}. In contrast, data compiled from published field and laboratory investigations of anaerobic ethylbenzene biodegradation was sufficient for the derivation of degradation rate values, as summarised in Figure 4.2. Although, the individual datapoints are not individually presented in Suraez & Rifai (1999), the derived ranges provide a useful benchmark that has been used in the derivation of UK rates in this project. No information on the effects of contaminant concentration on biodegradation rate were reported.

A similar survey of anaerobic biodegradation rates by Aronson & Howard (1997) reported mean first-order rate constant values from laboratory and field studies under denitrifying, iron-reducing, sulphate-reducing and methanogenic conditions to be 0.28 day^{-1}, 0.0011 day^{-1}, 0.0098 day^{-1}, and 0.05 day^{-1}, respectively. They suggested a range of rate constants to be applied in groundwater fate and transport models for anaerobic ethylbenzene plumes, namely 0.00060 day^{-1} (half-life of 1155 days), which was the lowest measured field value, to 0.015 day^{-1} (half-life of 46 days), which was the mean value for the entire field/*in situ* microcosm data set that they considered. No attempt was made by those authors to correlate rate with starting contaminant concentration; analysis of their dataset was made for this project but no clear correlation between concentration and rate could be discerned (Figure 4.5). There was little information on the effects of ethylbenzene concentration on biodegradation.

Xylenes

There are no significant abiotic degradation pathways for xylenes in groundwater.

The xylene isomers are biodegradable under both aerobic and anaerobic conditions (e.g., Suarez & Rifai, 1999; Beller *et al.*, 1992; Edwards *et al.*, 1992; Harms *et al.*, 1999; Haner *et al.*, 1995). The biodegradation of the three xylene isomers can differ significantly in any given environment. Generally, it has been found that *o*-xylene is the most difficult to biodegrade (Smith, 1993) but this is not invariably the case.

In a detailed survey of groundwater biodegradation rates, Suarez & Rifai (1999) compiled data from a number of published field and laboratory investigations of aerobic and anaerobic xylene biodegradation. These results are summarised in Figures 4.1 and 4.2. Although, the individual datapoints are not individually presented in Suraez & Rifai (1999), the derived ranges provide a useful benchmark that has been used in the derivation of UK rates in this

project. No information on the effects of contaminant concentration on biodegradation rate were reported.

A similar survey of anaerobic biodegradation rates by Aronson & Howard (1997) reported mean first-order rate constant values for the xylene isomers. Their data for laboratory and field studies for the three isomers were reported as:

- *o*-xylene: denitrifying = 0.12 day^{-1}; iron-reducing = 0.0052 day^{-1}; sulphate-reducing = 0.091 day^{-1}; methanogenic = 0.021 day^{-1}.
- *m*-xylene: denitrifying = 0.040 day^{-1}; iron-reducing = 0.0078 day^{-1}; sulphate-reducing = 0.065 day^{-1}; methanogenic = 0.021 day^{-1}.
- *p*-xylene: denitrifying = 0.047 day^{-1}; iron-reducing = 0.0050 day^{-1}; sulphate-reducing = 0.079 day^{-1}; methanogenic = 0.015 day^{-1}.

Based on field experience, they suggested a range of rate constants be applied in groundwater fate and transport models for anaerobic xylene plumes, as follows:

- *o*-xylene: 0.0012 day^{-1} (half-life of 578 days) to 0.016 day^{-1} (half-life of 43 days);
- *m*-xylene: 0.00082 day^{-1} (half-life of 845 days) to 0.021 day^{-1} (half-life of 33 days);
- *p*-xylene: 0.00085 day^{-1} (half-life of 815 days) to 0.015 day^{-1} (half-life of 46 days),

No attempt was made by those Aronson & Howard to correlate rate with starting contaminant concentration. Analysis of their dataset for this project (Figures 4.6-4.8) suggested that, for all isomers, increased biodegradation rate was weakly correlated with higher initial xylene concentrations, at least up to 30 mg l^{-1}.

There is little information on xylene concentrations causing inhibition of its own biodegradation, although effects have been noted at dissolved concentrations of 50 mg l^{-1} (Smith, 1993).

Interactions between BTEX components

The presence of mixtures of BTEX components in groundwater may impact their individual biodegradation in two ways:

- Preferential utilisation
- Toxicity

Preferential utilisation is where one or more BTEX components inhibit or prevent the biodegradation of the others until they have been largely eliminated. For example, Anderson & Lovley (1999) reported a case where the degradation of benzene in groundwater under iron-reducing conditions was completely inhibited until all toluene had been biodegraded. Similarly, Barlaz *et al.* (1995) observed that toluene inhibited the biodegradation of *m*-xylene and that both of these inhibited the degradation of benzene under iron-reducing, sulphate-reducing and methanogenic conditions. This effect was still manifested at toluene and xylene concentrations as low as a few mg l^{-1}. Such behaviour is not noted at all sites (e.g., see Newell & Connor, 1998).

There has been relatively little work undertaken on the toxicity to biodegradation of BTEX in mixtures. Experience reported as Case 2 of Appendix 8 suggests that total BTEX is likely to display inhibitory effects similar to the equivalent concentrations of benzene or xylenes, namely that inhibition may be expected to become significant at 50-100 mg l^{-1}.

4.1.2 Polycyclic aromatic hydrocarbons (PAH's)

Unlike BTEX, the fate of PAHs is strongly dependent on their sorption properties, particularly for the higher molecular weight compounds (see Section 4.3).

Naphthalene

There are no significant abiotic degradation pathways for naphthalene in groundwater.

Degradation has been shown potentially to occur under aerobic (e.g., Smith, 1993), denitrifying (Durant *et al.*, 1995), iron-reducing (Anderson & Lovley, 1999) and sulphate-reducing (Coates *et al.*, 1997; Zhang & Young, 1997) conditions.

A survey of anaerobic biodegradation rates by Aronson & Howard (1997) suggested a range of rate constants to be applied in groundwater fate and transport models for anaerobic naphthalene plumes, zero (i.e., no biodegradation) to 0.0072 day^{-1} (half-life of 96 days), which was the mean value for the entire field and *in situ* microcosm data set that they considered. No attempt was made by those authors to correlate rate with starting contaminant concentration. Plotting rate against concentration for this dataset (Figure 4.9) showed no clear correlation between concentration and rate could be discerned (Figure 4.9).

Due to the low bioavailability, no significant inhibitory effects of dissolved naphthalene on biodegradation are anticipated. Indeed, in soil and slurry systems, no detrimental effects of naphthalene were observed at concentrations of 900-1400 mg kg (dry weight soil)$^{-1}$ (Thierrin *et al.* 1995; Sims & Abbott, 1992), which would presumably give near-saturation concentrations in solution.

Benzo(a)pyrene

It should be noted that sorption of benzo(a)pyrene can be enhanced by biological processes that covalently incorporate partially oxidised biodegradation products into soil humus (Sims & Abbott, 1992).

There are no significant abiotic degradation pathways for benzo(a)pyrene in groundwater.

No publications were identified that specifically addressed the biodegradation of dissolved benzo(a)pyrene in groundwater, presumably due to the very low water solubility of this compound (<5 μg l^{-1} at 20ºC; Table 3.2); it has been shown that the biodegradation of this compound is very strongly controlled by bioavailability (Potter *et al.*, 1999; Johnson & Ghosh, 1998).

Benzo(a)pyrene has been shown to be biodegradable in soils and slurry systems under aerobic conditions (Smith, 1993) and some anaerobic conditions (denitrifying, sulphate reducing; Johnson & Ghosh, 1998).

Due to the low bioavailability, no significant inhibitory effects of dissolved benzo(a)pyrene on biodegradation are anticipated. Indeed, in soil and slurry systems, no detrimental effects of benzo(a)pyrene were observed at 126 mg kg (dry weight soil)$^{-1}$ (Sims & Abbott, 1992), which would presumably give near-saturation concentrations in solution.

4.1.3 Fuel additives

Methyl tert-butyl ether (MTBE)

There are no significant abiotic degradation pathways for MTBE in groundwater.

Early studies with MTBE reported that this compound was highly resistant to biodegradation in groundwater and in effluent treatment systems (see Environment Agency, 2000b). However, subsequent laboratory and field work has demonstrated that significant biodegradation of MTBE at concentrations up to 200 mg l^{-1} can take place under aerobic conditions (e.g., Salanitro *et al.*, 1994; Borden *et al.*, 1997; Church *et al.*, 2000; Bradley *et al.*, 1999) and anaerobic conditions, including iron-reducing (Landmeyer, 1998), denitrifying (e.g., Salanitro *et al.*, 1994; Borden *et al.*, 1997; Church *et al.*, 2000) and methanogenic (e.g., Mormile *et al.*, 1994; Wilson *et al.*, 2000). No reports were identified that unequivocally demonstrated MTBE biodegradation under sulphate-reducing conditions.

In a review of MTBE plume behaviour, Kolhatkar *et al.* (2000) reported that sites where significant MTBE biodegradation was observed were usually either predominantly aerobic or predominantly methanogenic. Sites where conditions in the plume favoured anaerobic biodegradation other than methanogenesis tended to exhibit insignificant MTBE degradation.

It should be noted that MTBE biodegradation is highly site-specific and that numerous reports fail to demonstrate significant biodegradation. In some cases, this has been attributed to interactions between the biodegradation of MTBE and petroleum hydrocarbon components, as discussed below.

The biodegradation pathway operating for MTBE involves conversion of MTBE to *tert*-butyl alcohol then degradation *via* isopropanol, *tert*-butyl formate and/or acetone to CO_2 (Church *et al.*, 1999). In some cases, biodegradation does not proceed beyond *tert*-butyl alcohol but this is site-specific.

The inhibitory effect of MTBE on its own biodegradation has been little studied – most papers naturally focus on the inhibition of MTBE biodegradation by BTEX (see discussion below). Certainly, a concentration of 200 mg l^{-1} has been shown to have no significant detrimental effect (Environment Agency, 2000b) and Daniel & Borden (1997) reported MTBE biodegradation in contaminant source areas under aerobic conditions.

Ethanol

Ethanol is not subject to significant chemical degradation in groundwater.

Ethanol biodegradation can take place readily under aerobic and all anaerobic conditions (Suflita & Mormile, 1993). In a review of biodegradation studies by Rice *et al.* (1999), half-lives for ethanol in laboratory microcosm studies were reported to be 1-3 days under aerobic conditions and no more than 7 days under anaerobic conditions.

Ethanol has very little inhibitory effect on its own biodegradation in groundwater. Rice *et al.* (1999) reviewed the available literature and concluded that only very high ethanol concentrations (at or above 50,000 mg l^{-1}) were likely to be inhibitory to most biodegradative organisms. These authors noted that dissolved ethanol at inhibitory concentrations would not result from releases of gasoline into groundwater, since the maximum amounts of ethanol used in US fuel formulations would give lower equilibrium concentrations. However, such concentrations could conceivably be reached from a release of pure ethanol.

Interactions between fuel additives and BTEX

Although there has been concern expressed in the past that gasoline fuel additives could conceivably enhance BTEX dissolution and transport in groundwater, evidence indicates that such effects do not take place at realistic additive concentrations. For example, Molson *et al.* (2000) reported that ethanol did not enhance BTEX dissolution or transport unless present in the source gasoline at >20% w/w. Similarly, Poulsen *et al.* (1992) and Davidson (1995) have shown that, when present in gasoline at concentrations below 15% w/w, MTBE does have a significant impact on BTEX transport or dissolution. In Europe, maximum MTBE concentrations are generally below 5% w/w and often around 1% w/w (Environment Agency 2000b). Ethanol is not normally present in gasoline sold in the UK.

The likely unimportance of these additives is reinforced by modelling studies performed by Rice *et al.* (1999), which found that the potential *worst-case* effect of ethanol would be to increase benzene plume length by less than a factor of two.

The biodegradation of MTBE under both aerobic and anaerobic conditions has regularly been found to be inhibited by the presence of BTEX, other petroleum hydrocarbon components and, indeed, other readily degradable contaminants (e.g., Yeh & Novak, 1995; Wilson & Cho, 2000; Wilson *et al.*, 2000). Indeed, Deeb *et al.* (2001) reported total inhibition of aerobic MTBE biodegradation in the presence of ethylbenzene or xylenes at 20 mg l^{-1} and a significant reduction of MTBE biodegradation by benzene and toluene at the same concentration. Conversely, there have been no reports of significant inhibition of BTEX biodegradation by MTBE in groundwater, presumably due to the relatively poor biodegradation of this oxygenate.

Ethanol has been shown to reduce the rate of aerobic benzene degradation when present at concentrations above 20 mg l^{-1} and to prevent it totally at 300 mg l^{-1} (Corseuil & Alvarez, 1996; Corseuil *et al.*, 1996). Molson *et al.* (2000) reported the effect of methanol (as a surrogate for ethanol) on aerobic BTEX biodegradation and obtained statistically significant depression of the rate of benzene, ethylbenzene and *p*-xylene. Hunt & Alvarez (1997) noted that initial ethanol concentrations of 100-300 mg l^{-1} were adequate to completely inhibit BTEX biodegradation in microcosms of aquifer material until the ethanol had been fully biodegraded. Conversely, there have been no reports of significant inhibition of ethanol biodegradation by BTEX in groundwater, presumably due to the ready degradability of ethanol.

4.1.4 Phenol

There are no significant abiotic degradation pathways for phenol in groundwater.

Biodegradation of phenol readily takes place under aerobic and the full range of anaerobic conditions (e.g., Smith, 1993; Thomas & Chiampo, 1998; Godsy *et al.*, 1992; Grbic-Galic, 1990; van Schie & Young, 2000).

Significant inhibition of biodegradation activity takes place at elevated dissolved concentrations in groundwater. For example, Harrison *et al.* (2001) and Lerner *et al.* (2000) reported significant reduction in aerobic phenol biodegradation rates in sandstone aquifer samples at 90-100 mg l^{-1} and total inhibition at 320 mg l^{-1}. Under predominantly sulphate-reducing anaerobic conditions, biodegradation was prevented at a phenol concentration of 90 mg l^{-1}. Similar results were reported for other aquifers by Presecan & Friesen (1999) and Broholm & Arvin (2000), who reported phenol biodegradation under both aerobic and anaerobic conditions could be significantly inhibited at concentrations above 60-70 mg l^{-1} but no significant effect at lower concentrations.

A survey of anaerobic biodegradation rates by Aronson & Howard (1997) suggested rate constants to be applied in groundwater fate and transport models for phenol plumes to be 0.0013 day^{-1} (a half-life of 533 days; which is an order of magnitude less than the lowest reported rate constant for a laboratory microcosm study) to 0.032 day^{-1} (a half-life of 22 days), which was the mean value for the field/*in situ* microcosm data set that they studied. No attempt was made by those authors to correlate rate with starting contaminant concentration; analysis of their dataset was made for this project but no clear correlation between concentration and rate could be discerned (Figure 4.10).

4.1.5 Pesticides

Mecoprop

There are no significant abiotic degradation mechanisms for Mecoprop in groundwater.

Mecoprop is one of a group of chlorophenoxyalkanoic acids that are chiral, i.e., the molecules can exist as two structures which are mirror images of each other and cannot be superimposed (Appendix 4). These enantiomers are designated (R)- and (S)-Mecoprop. Individual enantiomers have identical physical and chemical properties but their biochemical behaviour and effects can be very different. As Williams *et al.* (2001) have pointed out, this can be very useful in assessing natural attenuation, for example in the case where one enantiomer is readily biodegraded and the other not, then a clear change in the relative abundance of these enantiomers may occur along the plume. Note also, however, that biological interconversion of enantiomers may take place.

The differences in biochemical behaviour of the Mecoprop enantiomers makes interpretation of biodegradation data difficult. For example, it has been shown that 50% of added Mecoprop often biodegrades rapidly under aerobic conditions, followed by a much slower degradation of the remainder (Heron & Christensen, 1992). In most (but by no means all) cases, it is the (S)-form that is more readily biodegraded; the (R)-form is either biodegraded slowly or converted biologically into the (S)-form and then utilised (e.g., Zipper *et al.*, 1996 or 1998?; Müller & Buser, 1996; Kohler *et al.*, 1999). Under anaerobic conditions, most evidence suggests that

Mecoprop is persistent or, at best, extremely poorly biodegraded (e.g., Larsen *et al.*, 2000; Rügge *et al.*, 1999).

Williams *et al.* (2001) reported a detailed study of Mecoprop biodegradation in the Lincolnshire limestone aquifer at Helpston, northwest of Peterborough. Under aerobic conditions, they noted ready biodegradation of the (S)-enantiomer with kinetics exhibiting first-order behaviour. (R)-Mecoprop was only very slowly biodegraded. No biodegradation took place under anaerobic conditions; however, under iron-reducing or denitrifying conditions the bioconversion of (R)- to (S)-Mecoprop took place. Specific kinetics for the bioconversion reactions were not established for this site but kinetics from a comparable case in Switzerland described by Buser & Müller (1998) are illustrated in Figure 4.11.

It should also be noted that Johnson *et al.* (2000) studied the biodegradation of Mecoprop in microcosms of ground chalk from southern England and found no aerobic biodegradation at low concentrations (100 $\mu g\ l^{-1}$).

Parathion

Parathion is potentially subject to hydrolysis in aquatic systems, although Ragnarsdottir (2000) noted that rates of hydrolysis measured in the laboratory seriously overestimated the rate of abiotic degradation in soil and groundwater. This author suggested that appropriate hydrolysis half-life for parathion at 10ºC and pH 7.0-7.5 would be approximately 1 year. The main products of hydrolysis would be *p*-nitrophenol and diethyl-O-thiophosphate (Verschueren, 1996).

Parathion (O,O-diethyl-O-*p*-nitrophenylphosphorothioate) and its close relative methyl parathion (O,O-dimethyl-O-*p*-nitrophenylphosphorothioate) have been shown to be biodegraded under aerobic and anaerobic conditions (MacRae, 1989). Biodegradation proceeds through hydrolysis to *p*-nitrophenol and diethyl-O-thiophosphate, which can be further metabolised under both aerobic and anaerobic conditions (Verschueren, 1996).

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Inhibition of parathion biodegradation at elevated contaminant concentrations in groundwater was not expressly reported in the reviewed references, although testing using the commercial Microtox® method suggested inhibition of microbial activity may be significant at 5-10 $mg\ l^{-1}$ (DeLorenzo *et al.*, 2001).

4.1.6 Chlorinated solvents

Chlorinated solvent contamination that may be encountered in groundwater will commonly consist of one or more chlorinated compounds of methane, ethane or ethene compounds and, in many cases, partially dechlorinated degradation intermediates.

For the purposes of this report, a selection of the commonly encountered solvents and intermediates have been considered and their properties summarised using information provided in the numerous reviews in the literature, for example Wilson *et al.* (1997); Lee *et al.* (1998); Wiedemeier *et al.* (1998); Industrial members of the RTDF Bioremediation Consortium (1997); Lee *et al.*, 1998; Rijnaarts *et al.*, 1997.

Tetrachloroethene (PCE)

PCE is not subject to significant chemical degradation in groundwater.

PCE is not subject to any form of biodegradation under aerobic conditions.

Under anaerobic conditions, PCE cannot be used as a carbon and energy source. PCE can be biodegraded by reductive dechlorination (co-metabolism and/or dehalorespiration) under highly reducing conditions (sulphate-reducing, methanogenic) to yield TCE (with the potential for further step-wise biodegradation to ethene; Figure 4.12). Such reductive dechlorination is entirely dependent on the presence of biodegradable carbon and energy sources.

In a detailed survey of groundwater biodegradation rates, Suarez & Rifai (1999) compiled data from a number of published field and laboratory investigations of PCE anaerobic biodegradation. These results are summarised in Figure 4.13. Although, the individual datapoints are not individually presented in Suarez & Rifai (1999), the derived ranges provide a useful benchmark that has been used in the derivation of UK rates in this project.

A similar survey of anaerobic biodegradation rates by Aronson & Howard (1997) suggested an average rate constant to be applied in groundwater fate and transport models for PCE plumes undergoing reductive dechlorination, namely 0.0029 day^{-1} (half-life of 239 days), which was the mean value for the field/*in situ* microcosm data set that they studied and assumes that there remains an adequate supply of carbon and energy sources. No attempt was made by those authors to correlate rate with starting contaminant concentration; analysis of their dataset was made for this project but no clear correlation between concentration and rate could be discerned (Figure 4.14).

Trichloroethene (TCE)

TCE is not subject to significant chemical degradation in groundwater.

TCE cannot be utilised as a carbon and energy source under aerobic conditions.

TCE can be aerobically biodegraded by co-metabolism to CO_2 + H_2O + Cl^- by certain microorganisms utilising other organic compounds for growth (Figure 4.12). Substrates supporting TCE co-metabolism include methane, ethane, propane, butane, toluene and phenol. However, this pathway has not been shown to be a *major* process in MNA under groundwater

conditions since it relies on the simultaneous presence of the organic substrate, TCE and sufficient dissolved oxygen.

Under anaerobic conditions, TCE cannot be used as a carbon and energy source. TCE can be biodegraded by reductive dechlorination (co-metabolism and/or dehalorespiration) under highly reducing conditions (sulphate-reducing, methanogenic) to yield *cis*-1,2-DCE (with the potential for further biodegradation; Figure 4.12). Such reductive dechlorination is entirely dependent on the presence of biodegradable carbon and energy sources. It should be noted that the biological generation of DCE from TCE results in almost 100% of the *cis*- isomer; the presence of a significant proportion (>80%) of *cis*-1,2-DCE is therefore usually a strong indicator of reductive dechlorination.

In a detailed survey of groundwater biodegradation rates, Suarez & Rifai (1999) compiled data from a number of published field and laboratory investigations of TCE anaerobic biodegradation. These results are summarised in Figure 4.13. Although, the individual datapoints are not individually presented in Suraez & Rifai (1999), the derived ranges provide a useful benchmark that has been used in the derivation of UK rates in this project. No information on the effects of contaminant concentration on biodegradation rate were reported.

A similar survey of anaerobic biodegradation rates by Aronson & Howard (1997) suggested an average rate constants to be applied in groundwater fate and transport models for PCE plumes undergoing reductive dechlorination, namely 0.0025 day^{-1} (half-life of 277 days), which was the mean value for the field/*in situ* microcosm data set that they studied and assumes that there remains an adequate supply of carbon and energy sources. No attempt was made by those authors to correlate rate with starting contaminant concentration; analysis of their dataset was made for this project but no clear correlation between concentration and rate could be discerned (Figure 4.15).

Dichloroethene (DCE)

DCE isomers are not subject to significant chemical degradation in groundwater.

1,1-, *cis*-1,2- and *trans*-1,2-DCE isomers can be utilised as carbon and energy sources under aerobic conditions. (Mahaffey *et al.*, 1997; Bradley & Chapelle, 1998a).

DCE isomers can be aerobically biodegraded by co-metabolism to CO_2 + H_2O + Cl^- by microorganisms utilising certain other organic compounds for growth (Figure 4.12). Substrates supporting DCE co-metabolism include methane, ethane, propane, butane, toluene and phenol. However, this pathway is rarely a major process in MNA under groundwater conditions since it relies on the simultaneous presence of the organic substrate, DCE and sufficient dissolved oxygen.

Under anaerobic conditions, DCE can be used as a carbon and energy source under iron-reducing conditions (Wiedemeier *et al.*, 1997; Bradley & Chapelle, 1998b).

1,1-, *cis*-1,2- and *trans*-1,2-DCE isomers can often be biodegraded by reductive dechlorination (co-metabolism and/or dehalorespiration) under highly reducing conditions (sulphate-reducing, methanogenic) to yield vinyl chloride (with the potential for further biodegradation; Figure 4.12), provided that there is a supply of carbon and energy sources. Such reductive dechlorination is entirely dependent on the presence of biodegradable carbon and energy.

In a detailed survey of groundwater biodegradation rates, Suarez & Rifai (1999) compiled data from a number of published field and laboratory investigations of *cis*-1,2-DCE anaerobic biodegradation. These results are summarised in Figure 4.13. Although, the individual datapoints are not individually presented in Suraez & Rifai (1999), the derived ranges provide a useful benchmark that has been used in the derivation of UK rates in this project. No information on the effects of contaminant concentration on biodegradation rate were reported.

Vinyl chloride (VC)

There are no significant abiotic degradation pathways for vinyl chloride in groundwater.

VC can be utilised as a carbon and energy source under aerobic conditions (Davis & Carpenter, 1990; Bradley & Chapelle, 1998a).

VC can be aerobically biodegraded by co-metabolism to CO_2 + H_2O + Cl^- by certain microorganisms utilising other organic compounds (Figure 4.12). Substrates supporting VC co-metabolism include methane, ethane, propane, butane, toluene and phenol. However, this pathway is rarely a major process in MNA under groundwater conditions since it relies on the simultaneous presence of the organic substrate, VC and sufficient dissolved oxygen.

Under anaerobic conditions, VC can be used as a carbon and energy source under denitrifying (Leethem & Larson, 2000) and iron-reducing conditions (Wiedermeier *et al.*, 1997; Bradley & Chapelle, 1996; 1998b).

VC can also be biodegraded by reductive dechlorination (co-metabolism and/or dehalorespiration) under highly reducing conditions (sulphate-reducing, methanogenic) to yield ethene provided that there is a supply of carbon and energy sources. Such reductive dechlorination is entirely dependent on the presence of biodegradable carbon and energy. In some cases, a significant proportion of ethane and/or methane may be generated as a result of the reductive dechlorination of VC, which may complicate field mass balances of VC fate.

In a detailed survey of groundwater biodegradation rates, Suarez & Rifai (1999) compiled data from a number of published field and laboratory investigations of VC anaerobic biodegradation. These results are summarised in Figure 4.13. Although, the individual datapoints are not individually presented in Suraez & Rifai (1999), the derived ranges provide a useful benchmark that has been used in the derivation of UK rates in this project. No information on the effects of contaminant concentration on biodegradation rate were reported.

A similar survey of anaerobic biodegradation rates by Aronson & Howard (1997) concluded that there was not sufficient data available at that time to determine separate rate constants for biodegradation of vinyl chloride under denitrifying, iron-reducing, sulphate-reducing and methanogenic conditions. They therefore suggested a range of rate constants be applied in groundwater fate and transport models for anaerobic VC plumes, namely 0.00033 day^{-1} (half-life of 2100 days), which was the lowest measured field value (reported for methanogenic/sulphate-reducing conditions), to 0.0073 day^{-1} (half-life of 95 days), which was the mean value for the entire field/*in situ* microcosm data set that they considered. No attempt was made by those authors to correlate rate with starting contaminant concentration; analysis of their dataset was made for this project but no clear correlation between concentration and rate could be discerned (Figure 4.16).

Interactions between chlorinated ethenes

In view of the interdependence of the reductive dechlorination process in the attenuation of chlorinated ethenes, there has been significant work performed on their interactions. Results have been variable.

This is well illustrated by the survey of landfill leachate plumes reported by Kromann *et al.* (1998). These authors found that some sites showed no effect of PCE, TCE and DCE on reductive dechlorination of each other but that at other sites concentrations as low as 2 mg l^{-1} PCE was found to inhibit further dechlorination of TCE, which in turn inhibited further dechlorination of DCE.

More specifically, Nielsen & Keasling (1999) reported that the rate of reductive dechlorination of TCE was not significant affected by the presence of VC concentrations up to 31 mg l^{-1}. TCE only affected the biodegradation rate of DCE and VC when it was present at very high concentrations (around saturation). In this case, the rate of DCE reductive dechlorination *decreased* by a factor of 23 but the rate of VC dechlorination *increased* by a factor of 120. A similar result was obtained by Distefano (1999) who found that the rate of VC dechlorination was up to 10 times greater in the presence of PCE (57 μg l^{-1}) than in its absence. This may suggest that the rate of VC reductive dechlorination could reduce at plume margins once the more highly dechlorinated solvents have been eliminated. However, since VC can be utilised as a carbon and energy source under aerobic and certain anaerobic conditions, this issue may not arise at a significant proportion of sites.

It is important to emphasis that reductive dechlorination processes (whether co-metabolism or dehalorespiration) require the presence of organic carbon and energy sources for their operation. Appropriate "carbon and energy source" sources include natural organic matter, landfill leachate (e.g., Kromann *et al.*, 1998; Thornton *et al.*, 2000) alcohols, ketones, BTEX and other petroleum hydrocarbons (e.g., Cox & Major, 1993; Major *et al.*, 1991; Weaver *et al.*, 1997), chlorinated organics (e.g., dichloropropane; Hardy *et al.*, 1999). It is therefore essential that potential carbon and energy sources are evaluated when reductive dechlorination is a significant attenuation process.

Effects of chlorinated ethene concentration on biodegradation

There has been a significant amount of recent work looking at the effects of saturation concentrations of chlorinated solvents on reductive dechlorination. Unlike most dissolved phase contaminants described above, it appears that chlorinated ethene biodegradation is not generally inhibited at elevated contaminant concentrations.

Nielsen & Keasling (1999), Lee *et al.* (1999), Isalou *et al.* (1998) and Yang & McCarty (2000) found no inhibitory effect of very high to saturating concentrations of PCE or TCE on reductive dechlorination, even when free-phase organic was present. It should be noted that the degradation is restricted to the dissolved chlorinated solvent and not to the free-phase itself. Similarly, Carr *et al.* (2000) evaluated reductive dechlorination in a system containing a free-phase chlorinated solvent mixture comprising PCE, TCE, DCE and 1,1,1-TCA. Again, there was no significant effect on reductive dechlorination. Indeed, Yang & McCarty (2000) have found that the presence of free-phase PCE and the high concentrations of intermediates generated during its reductive dechlorination can actually increase the rate of reductive dechlorination by inhibiting the growth of competing organisms in aquifer sediment.

No significant information is available on the inhibitory effect of elevated contaminant concentrations on direct aerobic or anaerobic biodegradation of chlorinated solvents.

Trichloroethane (TCA)

1,1,1-Trichloroethane is the only major chlorinated solvent that can be transformed chemically in groundwater at a significant rate. Transformation occurs by two different pathways operating simultaneously (Figure 4.17), leading to the formation of 1,1-DCE and acetic acid. The rates of these two reactions differ such that the yield of these different products under groundwater conditions is generally 20-30% 1,1-DCE and 70-80% acetic acid (Wing, 1997). The half-life of 1,1,1-TCA has been reported from various field and laboratory studies to be 0.5-1.1 years at 25ºC; 1.7-3.8 years at 20ºC and 2.0-2.9 years at 15ºC (Wing, 1997). The abiotic degradation half-life of 1,1,2-trichloroethane in groundwater is in the order of 150 years (Wiedemeier *et al.*, 1998) and therefore not significant from the viewpoint of MNA.

It should be noted that acetic acid is readily biodegraded under aerobic and all anaerobic conditions and may therefore be difficult to detect under field conditions. 1,1-DCE is biodegradable but at a slower rate and its presence in a significant proportion is often a good marker of abiotic 1,1,1-TCA degradation, unless there are other reasons for its presence.

TCA isomers cannot be utilised as carbon and energy sources (direct biodegradation as "carbon and energy source") under aerobic conditions but can be biodegraded aerobically by co-metabolism to CO_2 + H_2O + Cl^- by certain microorganisms utilising other organic compounds for growth. Substrates supporting TCA co-metabolism include methane, ethane, propane, butane, toluene and phenol. However, this pathway is rarely a major process in MNA under groundwater conditions since it relies on the simultaneous presence of the organic substrate, TCA and sufficient dissolved oxygen.

Under anaerobic conditions, TCA isomers cannot be used as a carbon and energy source but can be biodegraded by reductive dechlorination (co-metabolism and/or dehalorespiration) under highly reducing conditions (sulphate-reducing, methanogenic; Klecka *et al.*, 1990) to yield DCA isomers (with the potential for further biodegradation). Such reductive dechlorination is entirely dependent on the presence of biodegradable carbon and energy sources.

In a detailed survey of groundwater biodegradation rates, Suarez & Rifai (1999) compiled data from a number of published field and laboratory investigations of TCA anaerobic biodegradation. These results are summarised in Figure 4.13. Although no specific judgement can be made on the validity of the individual data points in these compilations, they provide a useful benchmark for validation of the data extracted from the references reviewed in this project. No information on the effects of contaminant concentration on biodegradation rate were reported.

Dichloroethane (DCA)

There are no significant abiotic degradation pathways for DCA isomers in groundwater.

1,2-DCA can be utilised as a carbon and energy source (direct biodegradation as "carbon and energy source") under aerobic conditions (Klecka *et al.*, 1998; Stucki *et al.*, 1992; Cox *et al.*, 2000).

DCA can be aerobically biodegraded by co-metabolism to CO_2 + H_2O + Cl^- by certain microorganisms utilising other organic compounds for growth. Substrates supporting DCA co-metabolism include methane, ethane, propane, butane, toluene and phenol. However, this pathway is rarely a major process in MNA under groundwater conditions since it relies on the simultaneous presence of the organic substrate, DCA and sufficient dissolved oxygen.

Under anaerobic conditions, DCA isomers can be used as a carbon and energy source under denitrifying, manganese-reducing and iron-reducing conditions (Klecka *et al.*, 1998; Cox *et al.*, 2000. DCA isomers can also be biodegraded by reductive dechlorination (co-metabolism and/or dehalorespiration) under highly reducing conditions (sulphate-reducing, methanogenic; Maymo-Gatell *et al.*, 1999; Klecka *et al.*, 1998; Cox *et al.*, 2000) to yield ethene. Such reductive dechlorination is entirely dependent on the presence of biodegradable carbon and energy. It is worth noting that the chloroethane produced by reductive dechlorination of DCA is rapidly hydrolysed by abiotic reactions to yield ethanol, which is rapidly biodegradable.

In a detailed survey of groundwater biodegradation rates, Suarez & Rifai (1999) compiled data from a number of published field and laboratory investigations of DCA anaerobic biodegradation. These results are summarised in Figure 4.13. Although no specific judgement can be made on the validity of the individual data points in these compilations, they provide a useful benchmark for validation of the data extracted from the references reviewed in this project. No information on the effects of contaminant concentration on biodegradation rate were reported.

Cox *et al.* (2000) reported no inhibitory effects of DCA on its own biodegradation under aerobic conditions at up to 500 mg l^{-1} and under methanogenic conditions at up to 800 mg l^{-1}.

4.1.7 Cyanide

Inorganic “cyanide” encountered as groundwater contamination may include the cyanide anion itself (CN^-), cyanate and thiocyanate anions (CNO^- and CNS^-) and iron cyanide complexes (Table 4.1; Kjeldsen, 1999).

Table 4.1. Forms of inorganic cyanide most commonly encountered at contaminated sites.

Form	Examples	Significance
Cyanide	CN-	Potential contaminant from electroplating works
Cyanates	Cyanate, thiocyanate	Contaminant at gasworks sites
Iron-complexed cyanides	"Blue Billy" Iron ferrocyanide ($Fe_4(Fe(CN)_6)_3$) Sodium ferrocyanide ($Na_4Fe(CN)_6$)	Common contaminant at gasworks sites Complexed cyanates and thiocyanates also common.

The fate of cyanides in groundwater is complex because cyanides have the potential to undergo a wide variety of reactions in the subsurface (Figure 4.18).

Iron-complexed cyanides exist in two oxidation forms (ferro- and ferricyanides) and can be transformed from one to the other only under the appropriate redox conditions. This is not a significant attenuation mechanism in groundwater due to the insignificant differences in hazard posed by these two species. The decomposition of complexed cyanide to yield free CN^- is energetically favourable but requires a large activation energy and is not a significant process in groundwater under *in situ* conditions (half-life for the decomposition of iron-cyanide complexes to cyanide by abiotic processes is in the order of 100-1000 years or greater; Kjeldsen, 1999).

Biological transformation of cyanides can occur under both aerobic and anaerobic conditions. Most data relate to CN^- itself, which can be utilised as a source of both carbon and nitrogen by microorganisms and can be mineralised to CO_2 + inorganic nitrogen species (e.g., Kjeldsen, 1999; Pereira *et al.*, 1996). CN^- can also be bioconverted to cyanate and thiocyanate, which can in turn be mineralised (Ecke *et al.*, 1993; Boucabeille *et al.*, 1994). With adapted microbial populations, tolerance to >100 mg CN^- l^{-1} has been reported (e.g., Meehan *et al.*, 1999) but very few papers report rates in a form suitable for extrapolation to MNA evaluations.

Microbial destruction of iron-complexed cyanides has also been reported, yielding iron salts, inorganic nitrogen species and CO_2 (e.g., Aronstein *et al.*, 1995; Babu *et al.*, 1996). Part of the reaction process is due to abiotic reactions and part to biological activity. However, this degradation appears to be site specific (e.g., Ghosh *et al.*, 1997)

4.2 Derived UK rates of attenuation by chemical and biological degradation

The intention of this section of the report is to provide guidance on the application of degradative attenuation process data in MNA evaluation, with particular reference to the effect of contaminant concentration and common UK aquifer conditions.

Lower and upper limits to biodegradation have been derived based on the literature reviewed in Section 4.1. The lower limits are generally more uncertain, being based on a smaller dataset, with experimental results often dictated by analytical detection limits.

Evaluation of the data presented in Appendices 5 and 6 to this report and the compilation publications reviewed above indicate that there is a very large range in measured degradation values within the normal concentration range within which biodegradation of a specific

contaminant occurs. These variations remain equally large for the specific geological formations in which the most rate data have been determined (unconsolidated sand & gravel aquifers in the United States).

The lack of a significant dataset for most contaminants in consolidated aquifers has made read-across of potential rate data to the major UK aquifers extremely uncertain and reliant upon generalisations. Outline guidance is therefore given based on the datasets associated with UK conditions and their known biogeochemical properties. It is emphasised that caution should be exercised if non-site specific laboratory or field data are being used to extrapolate degradation rates.

For convenience of reference, the recommendations are presented in tabular form for each contaminant under review, corrected to 10ºC and for two generalised aquifer types: shallow sand-gravel aquifers and UK consolidated formations. The tables summarise for each potential degradation process:

- whether degradation by that mechanism is considered likely to take place; and if so:
- the potential lower limit below which biodegradation will not take place or is likely to cease;
- the potential upper concentration limit at which significant inhibition of biodegradation is likely to be observed;
- the typical half-life of that contaminant under the defined conditions within the tolerable concentration range;
- comments and cautions.

4.2.1 Benzene, toluene, ethylbenzene and xylenes (BTEX)

The derived data for BTEX components are given in Tables 4.2- 4.5.

The reported interactions between BTEX components on their biodegradation in groundwater are inconsistent. There are cases where components inhibit degradation of others are known but no consistent patterns emerge from the literature; evaluate on case-specific basis where possible.

There is evidence to suggest that the potential onset of inhibition of BTEX mixtures may be apparent at total concentrations of >50 mg l^{-1}.

Table 4.2. Derived data for benzene attenuation by chemical and biological degradation.

Benzene – shallow sand/gravel aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	t½ = 50-350 days	50-100 mg l^{-1}	No clear relationship between concentration and rate
	Anaerobic	Denitrifying	1 μg l^{-1}	t½ = 100-500 days	50-100 mg l^{-1}	*Frequently no degradation – site-specific* No clear relationship between concentration and rate
		Iron-reducing	1 μg l^{-1}	t½ = 100-500 days	50-100 mg l^{-1}	
		Sulphate-reducing	1μg l^{-1}	t½ = 100-500 days	50-100 mg l^{-1}	
		Methanogenic	1 μg l^{-1}	t½ = 100-200 days	50-100 mg l^{-1}	
Benzene – Considerations for consolidated aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	Insufficient data; recommend site-specific test	50-100 mg l^{-1}	
	Anaerobic	Denitrifying	1 μg l^{-1}	Insufficient data; recommend site-specific test	50-100 mg l^{-1}	
		Iron-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific test	50-100 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific test	50-100 mg l^{-1}	
		Methanogenic	1 μg l^{-1}	Insufficient data; recommend site-specific test	50-100 mg l^{-1}	

Table 4.3. Derived data for toluene attenuation by chemical and biological degradation.

Toluene – shallow sand/gravel aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	$t_{½}$ = 20-200 days	200 mg l^{-1}	No clear relationship between concentration and rate
	Anaerobic	Denitrifying	1 μg l^{-1}	$t_{½}$ = 50-300 days	200 mg l^{-1}	*Frequently no degradation – site-specific* No clear relationship between concentration and rate
		Iron-reducing	1 μg l^{-1}	$t_{½}$ = 50-300 days	200 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	$t_{½}$ = 50-300 days	200 mg l^{-1}	
		Methanogenic	1 μg l^{-1}	$t_{½}$ = 50-2 300 days	200 mg l^{-1}	

Toluene – Considerations for consolidated aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	Insufficient data; recommend site-specific test	200 mg l^{-1}	
	Anaerobic	Denitrifying	1 μg l^{-1}	Insufficient data; recommend site-specific test	200 mg l^{-1}	
		Iron-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific test	200 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific test	200 mg l^{-1}	
		Methanogenic	1 μg l^{-1}	Insufficient data; recommend site-specific test	200 mg l^{-1}	

Table 4.4. Derived data for ethylbenzene attenuation by chemical and biological degradation.

Ethylbenzene – shallow sand/gravel aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	$t_{½}$ = 50-200 days	50-100 mg l^{-1}	No clear relationship between concentration and rate
	Anaerobic	Denitrifying	1 μg l^{-1}	$t_{½}$ = 200-800 days	50-100 mg l^{-1}	*Frequently no degradation – site-specific* No clear relationship between concentration and rate
		Iron-reducing	1 μg l^{-1}	$t_{½}$ = 200-800 days	50-100 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	$t_{½}$ = 200-800 days	50-100 mg l^{-1}	
		Methanogenic	1 μg l^{-1}	$t_{½}$ = 200-800 days	50-100 mg l^{-1}	

Ethylbenzene – Considerations for consolidated aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	Insufficient data; recommend site-specific data	50-100 mg l^{-1}	
	Anaerobic	Denitrifying	1 μg l^{-1}	Insufficient data; recommend site-specific data	50-100 mg l^{-1}	
		Iron-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific data	50-100 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific data	50-100 mg l^{-1}	
		Methanogenic	1 μg l^{-1}	Insufficient data; recommend site-specific data	50-100 mg l^{-1}	

Table 4.5. Derived data for xylene attenuation by chemical and biological degradation.

Xylenes – shallow sand/gravel aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	t½ = 50-200 days	50-100 mg l^{-1}	No clear relationship between concentration and rate Isomers can differ but not consistent
	Anaerobic	Denitrifying	1 μg l^{-1}	t½ = 100-500 days	50-100 mg l^{-1}	Frequently no degradation – site-specific Rate may increase with increasing concentration; No clear relationship between concentration and rate Isomers can differ but not consistent
		Iron-reducing	1 μg l^{-1}	t½ = 100-500 days	50-100 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	t½ = 100-500 days	50-100 mg l^{-1}	
		Methanogenic	1 μg l^{-1}	t½ = 100-500 days	50-100 mg l^{-1}	

Xylenes – Considerations for consolidated aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	Insufficient data; recommend site-specific data	50-100 mg l^{-1}	
	Anaerobic	Denitrifying	1 μg l^{-1}	Insufficient data; recommend site-specific data	50-100 mg l^{-1}	
		Iron-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific data	50-100 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific data	50-100 mg l^{-1}	
		Methanogenic	1 μg l^{-1}	Insufficient data; recommend site-specific data	50-100 mg l^{-1}	

4.2.2 Polycyclic aromatic hydrocarbons

The derived data for naphthalene is given in Table 4.6.

Data for benzo(a)pyrene are not presented as there are no chemical degradation mechanisms and its extremely low solubility of this compound means that there are no data on the dissolved phase biodegradation of this compound.

Table 4.6. Derived data for naphthalene attenuation by chemical and biological degradation.

Naphthalene – shallow sand/gravel aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		10 μg l^{-1}	t½ = 100-300 days	Above solubility	Significant slowing likely at low concentrations due to bioavailability constraints
	Anaerobic	Denitrifying	10 μg l^{-1}	t½ = 200-1000 days	Above solubility	*Frequently no degradation – site-specific* Significant slowing likely at low concentrations due to bioavailability constraints
		Iron-reducing	10 μg l^{-1}	t½ = 200-1000 days	Above solubility	
		Sulphate-reducing	10 μg l^{-1}	t½ = 200-1000 days	Above solubility	
		Methanogenic	Not confirmed			

Naphthalene – Considerations for consolidated aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		10 μg l^{-1}	Insufficient data; recommend site-specific data	Above solubility	
	Anaerobic	Denitrifying	10 μg l^{-1}	Insufficient data; recommend site-specific data	Above solubility	
		Iron-reducing	10 μg l^{-1}	Insufficient data; recommend site-specific data	Above solubility	
		Sulphate-reducing	10 μg l^{-1}	Insufficient data; recommend site-specific data	Above solubility	
		Methanogenic	10 μg l^{-1}	Insufficient data; recommend site-specific data	Above solubility	

4.2.3 Fuel additives

The derived data for MTBE and ethanol are given in Tables 4.7 and 4.8, respectively.

Studies of the effects of fuel additives on BTEX solubility have shown no enhancement of BTEX dissolution and solubility at the concentrations of additives encountered in gasoline.

Fuel additives and BTEX may have significant effects on each others' biodegradation:

- MTBE biodegradation may be reduced or stopped by BTEX at >10 mg l^{-1};
- BTEX biodegradation may be reduced or stopped by ethanol at >10 mg l^{-1}.

4.2.4 Phenol

The derived data for phenol is given in Table 4.9.

4.2.5 Pesticides

The derived data for Mecoprop and parathion are given in Tables 4.10 and 4.11, respectively.

4.2.6 Chlorinated solvents

The derived data for PCE, TCE, DCE, vinyl chloride and Mecoprop and parathion are given in Tables 4.12, 4.13, 4.14, 4.15 and 4.16, respectively.

For 1,1,1-TCA, it is very difficult to distinguish chemical from biological degradation in the field. Therefore it is recommended to base loss estimates on the chemical degradation rates which would give a typical groundwater half-life for 1,1,1-TCA of 3-4 years at 10ºC and pH 6-8.

Studies on the effects of chlorinated solvents on each others' biodegradation have been inconsistent; cases have been reported where they enhance, decrease or have no effect on rate. Where this is considered a potential issue for resolution at a specific site, then field data should be evaluated to determine potential interactions.

4.2.7 Inorganic cyanides

The chemical interconversion of free and complexed cyanides makes it impossible to derive simple relationships between concentration and biodegradation rate. Both aerobic and anaerobic biodegradation of CN^- in groundwater has been reported at concentrations up to 10 mg l^{-1}. Maximum tolerable concentrations have been found to vary greatly between sites; there have been cases where significant CN^- biodegradation has continued up to *circa* 100 mg l^{-1} but at others, inhibition has been marked above 10 mg l^{-1}.

Table 4.7. Derived data for MTBE attenuation by chemical and biological degradation.

MTBE – shallow sand/gravel aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1μg l^{-1}	$t_{½}$ = 100-1000 days	Above 200 mg l^{-1}?	*Frequently no degradation – site-specific* No clear relationship between concentration and rate
	Anaerobic	Denitrifying	1μg l^{-1}	$t_{½}$ = 200-2000 days	Above 200 mg l^{-1}?	*Frequently no degradation – site-specific* No clear relationship between concentration and rate
		Iron-reducing	1μg l^{-1}	$t_{½}$ = 200-2000 days	Above 200 mg l^{-1}?	
		Sulphate-reducing	1μg l^{-1}	$t_{½}$ = 200-2000 days	Above 200 mg l^{-1}?	
		Methanogenic	1μg l^{-1}	$t_{½}$ = 200-2000 days	Above 200 mg l^{-1}?	

MTBE – Considerations for consolidated aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	Insufficient data; recommend site-specific test	Above 200 mg l^{-1}?	
	Anaerobic	Denitrifying	1 μg l^{-1}	Insufficient data; recommend site-specific test	Above 200 mg l^{-1}?	
		Iron-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific test	Above 200 mg l^{-1}?	
		Sulphate-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific test	Above 200 mg l^{-1}?	
		Methanogenic	1 μg l^{-1}	Insufficient data; recommend site-specific test	Above 200 mg l^{-1}?	

Table 4.8. Derived data for ethanol attenuation by chemical and biological degradation.

Ethanol– shallow sand/gravel aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	$t_{½}$ = 10-100 days	>50000 mg l^{-1}	No clear relationship between concentration and rate
	Anaerobic	Denitrifying	1 μg l^{-1}	$t_{½}$ = 10-100 days	>50000 mg l^{-1}	No clear relationship between concentration and rate
		Iron-reducing	1 μg l^{-1}	$t_{½}$ = 10-100 days	>50000 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	$t_{½}$ = 10-100 days	>50000 mg l^{-1}	
		Methanogenic	1 μg l^{-1}	$t_{½}$ = 10-100 days	>50000 mg l^{-1}	

Ethanol – Considerations for consolidated aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	Insufficient data; recommend site-specific data	>50000 mg l^{-1}	
	Anaerobic	Denitrifying	1 μg l^{-1}	Insufficient data; recommend site-specific data	>50000 mg l^{-1}	
		Iron-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific data	>50000 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific data	>50000 mg l^{-1}	
		Methanogenic	1 μg l^{-1}	Insufficient data; recommend site-specific data	>50000 mg l^{-1}	

Table 4.9. Derived data for phenol attenuation by chemical and biological degradation.

Phenol – shallow sand/gravel aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	$t_{½}$ = 10-100 days	50-100 mg l^{-1}	No clear relationship between concentration and rate
	Anaerobic	Denitrifying	1 μg l^{-1}	$t_{½}$ = 50-300 days	50-100 mg l^{-1}	No clear relationship between concentration and rate
		Iron-reducing	1 μg l^{-1}	$t_{½}$ = 50-300 days	50-100 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	$t_{½}$ = 50-300 days	50-100 mg l^{-1}	
		Methanogenic	1 μg l^{-1}	$t_{½}$ = 50-300 days	50-100 mg l^{-1}	

Phenol – Considerations for consolidated aquifers (based on Triassic Sandstone data)						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	$t_{½}$ = 10-100 days	50-100 mg l^{-1}	Based on Triassic sandstone data
	Anaerobic	Denitrifying	1 μg l^{-1}	$t_{½}$ = 50-300 days	50-100 mg l^{-1}	Based on Triassic sandstone data
		Iron-reducing	1 μg l^{-1}	$t_{½}$ = 50-300 days	50-100 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	$t_{½}$ = 50-300 days	50-100 mg l^{-1}	
		Methanogenic	1 μg l^{-1}	$t_{½}$ = 50-300 days	50-100 mg l^{-1}	

Table 4.10. Derived data for Mecoprop attenuation by chemical and biological degradation.

Mecoprop – shallow sand/gravel aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	t½ = 50-350 days	50-100 mg l^{-1}	No clear relationship between concentration and rate Enantiomer conversion important
	Anaerobic	Denitrifying	No degradation			
		Iron-reducing	No degradation			
		Sulphate-reducing	No degradation			
		Methanogenic	No degradation			

Mecoprop – Considerations for consolidated aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	Insufficient data; recommend site-specific test	50-100 mg l^{-1}	Chalk data for lower limit Enantiomer conversion probably important
	Anaerobic	Denitrifying	No degradation			
		Iron-reducing	No degradation			
		Sulphate-reducing	No degradation			
		Methanogenic	No degradation			

Table 4.11. Derived data for parathion attenuation by chemical and biological degradation.

Parathion – shallow sand/gravel aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		t½ = 350-700 days			pH 6-8
Biodegradation	Aerobic		10 μg l^{-1}	t½ = 50-350 days	50-100 mg l^{-1}	No clear relationship between concentration and rate
	Anaerobic	Denitrifying	10 μg l^{-1}	t½ = 100-500 days	50-100 mg l^{-1}	No clear relationship between concentration and rate
		Iron-reducing	10 μg l^{-1}	t½ = 100-500 days	50-100 mg l^{-1}	
		Sulphate-reducing	10 μg l^{-1}	t½ = 100-500 days	50-100 mg l^{-1}	
		Methanogenic	10 μg l^{-1}	t½ = 100-200 days	50-100 mg l^{-1}	

Parathion – Considerations for consolidated aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		10 μg l^{-1}	Insufficient data; recommend site-specific test	50-100 mg l^{-1}	
	Anaerobic	Denitrifying	10 μg l^{-1}	Insufficient data; recommend site-specific test	50-100 mg l^{-1}	
		Iron-reducing	10 μg l^{-1}	Insufficient data; recommend site-specific test	50-100 mg l^{-1}	
		Sulphate-reducing	10 μg l^{-1}	Insufficient data; recommend site-specific test	50-100 mg l^{-1}	
		Methanogenic	10 μg l^{-1}	Insufficient data; recommend site-specific test	50-100 mg l^{-1}	

Table 4.12. Derived data for PCE attenuation by chemical and biological degradation.

PCE – shallow sand/gravel aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		No degradation			
	Anaerobic	Denitrifying	No degradation			
		Iron-reducing	No degradation			
		Sulphate-reducing	1 μg l^{-1}	$t½$ = 100-1000 days	Above solubility	*Requires co-contaminants to support reductive dechlorination* No clear relationship between concentration and rate
		Methanogenic	1 μg l^{-1}	$t½$ = 100-1000 days	Above solubility	

PCE – Considerations for consolidated aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		No degradation			
	Anaerobic	Denitrifying	No degradation			
		Iron-reducing	No degradation			
		Sulphate-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific test	Above solubility	*Requires co-contaminants to support reductive dechlorination*
		Methanogenic	1 μg l^{-1}	Insufficient data; recommend site-specific test	Above solubility	

Table 4.13. Derived data for TCE attenuation by chemical and biological degradation.

TCE – shallow sand/gravel aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		No degradation			
	Anaerobic	Denitrifying	No degradation			
		Iron-reducing	No degradation			
		Sulphate-reducing	1 μg l^{-1}	$t_{½}$ = 100-1000 days	Above solubility	*Requires co-contaminants to support reductive dechlorination* No clear relationship between concentration and rate
		Methanogenic	1 μg l^{-1}	$t_{½}$ = 100-1000 days	Above solubility	

TCE – Considerations for consolidated aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		No degradation			
	Anaerobic	Denitrifying	No degradation			
		Iron-reducing	No degradation			
		Sulphate-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific test	Above solubility	*Requires co-contaminants to support reductive dechlorination*
		Methanogenic	1 μg l^{-1}	Insufficient data; recommend site-specific test	Above solubility	

Table 4.14. Derived data for DCE attenuation by chemical and biological degradation.

DCE – shallow sand/gravel aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	$t_{½}$ = 50-350 days	>500 mg l^{-1}	No clear relationship between concentration and rate
	Anaerobic	Denitrifying	1 μg l^{-1}	$t_{½}$ = 500-3000 days	>500 mg l^{-1}	No clear relationship between concentration and rate
		Iron-reducing	1 μg l^{-1}	$t_{½}$ = 500-3000 days	>500 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	$t_{½}$ = 200-1000 days	>500 mg l^{-1}	*Requires co-contaminants to support reductive dechlorination*
		Methanogenic	1 μg l^{-1}	$t_{½}$ = 200-1000 days	>500 mg l^{-1}	

DCE – Considerations for consolidated aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	Insufficient data; recommend site-specific test	>500 mg l^{-1}	
	Anaerobic	Denitrifying	1 μg l^{-1}	Insufficient data; recommend site-specific test	>500 mg l^{-1}	
		Iron-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific test	>500 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific test	>500 mg l^{-1}	*Requires co-contaminants to support reductive dechlorination*
		Methanogenic	1 μg l^{-1}	Insufficient data; recommend site-specific test	>500 mg l^{-1}	

Table 4.15. Derived data for vinyl chloride attenuation by chemical and biological degradation.

VC – shallow sand/gravel aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	t½ = 50-200 days	>500 mg l^{-1}	No clear relationship between concentration and rate
	Anaerobic	Denitrifying	1 μg l^{-1}	t½ = 100-300 days	>500 mg l^{-1}	No clear relationship between concentration and rate
		Iron-reducing	1 μg l^{-1}	t½ = 100-300 days	>500 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	t½ = 100-500 days	>500 mg l^{-1}	*Requires co-contaminants to support reductive dechlorination*
		Methanogenic	1 μg l^{-1}	t½ = 100-500 days	>500 mg l^{-1}	

VC – Considerations for consolidated aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	Insufficient data; recommend site-specific test	>500 mg l^{-1}	
	Anaerobic	Denitrifying	1 μg l^{-1}	Insufficient data; recommend site-specific test	>500 mg l^{-1}	
		Iron-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific test	>500 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific test	>500 mg l^{-1}	*Requires co-contaminants to support reductive dechlorination*
		Methanogenic	1 μg l^{-1}	Insufficient data; recommend site-specific test	>500 mg l^{-1}	

Table 4.16. Derived data for DCA attenuation by chemical and biological degradation.

DCA isomers – shallow sand/gravel aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	t½ =100-500 days	>500 mg l^{-1}	No clear relationship between concentration and rate
	Anaerobic	Denitrifying	1 μg l^{-1}	>500 mg l^{-1}	>500 mg l^{-1}	No clear relationship between concentration and rate
		Iron-reducing	1 μg l^{-1}	>500 mg l^{-1}	>500 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	>800 mg l^{-1}	>800 mg l^{-1}	*Requires co-contaminants to support reductive dechlorination*
		Methanogenic	1 μg l^{-1}	>800 mg l^{-1}	>800 mg l^{-1}	

DCA isomers – Considerations for consolidated aquifers						
Attenuation process	**Biogeochemical conditions**		**Potential process performance**			**Comments**
			Lower limit	**Normal range**	**Upper limit**	
Abiotic degradation	All		No degradation			
Biodegradation	Aerobic		1 μg l^{-1}	Insufficient data; recommend site-specific test	>500 mg l^{-1}	
	Anaerobic	Denitrifying	1 μg l^{-1}	Insufficient data; recommend site-specific test	>500 mg l^{-1}	
		Iron-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific test	>500 mg l^{-1}	
		Sulphate-reducing	1 μg l^{-1}	Insufficient data; recommend site-specific test	>800 mg l^{-1}	*Requires co-contaminants to support reductive dechlorination*
		Methanogenic	1 μg l^{-1}	Insufficient data; recommend site-specific test	>800 mg l^{-1}	

4.3 Attenuation by sorption

4.3.1 Introduction

Section 3 briefly described the main sorption processes with details presented in Appendix 2. This section presents a review of the literature collected during this project relating to sorption with particular emphasis on the effects of contaminant concentration for the list of contaminants selected. The results of the literature search appear to reflect the complexity of the various problems associated with assessment of sorption processes at contaminated sites.

Two key points should be noted in relation to addressing sorption issues in this report:

- if the magnitude of sorption varies with contaminant concentration, then it is to be expected that a nonlinear model would best describe the sorption behaviour. Published assessments of data using nonlinear sorption models (especially freudlich sorption) have been identified and are mainly found in section 4.3.7 (chlorinated solvents);

- Although examples of non-equilibrium sorption are briefly reviewed, this report is primarily concerned with the extent rather than the rate of sorption processes.

This introduction has been split into the following sub-topics in order to deal with different aspects of sorption identified in the literature:

- Nonlinear sorption and the influence of contaminant concentration on sorption processes
- Influence of dissolved organic matter (DOM)
- Competitive and co-operative sorption
- Desorption – non-equilibrium sorption and residence time
- Sorption to organic carbon or mineral matter
- Quantity and type of f_{oc}

In the following sub-sections, the results of the literature review are presented on a contaminant group basis. A summary of the literature collated relating to sorption can be found in Appendix 6. The different sub-topics listed above and discussed below are considered within the contaminant group sections as and when they have been identified in the literature.

Nonlinear sorption and the influence of contaminant concentration on sorption processes

A linear sorption model assumes that the sorption partitioning process is independent of concentration and the distribution coefficient is a constant throughout a large range of concentrations. This approach has been documented as valid for a number of studies in various circumstances especially at low concentrations of contaminants and for more hydrophobic compounds. However, there are circumstances in which nonlinear Freundlich sorption has been reported to simulate experimental data more accurately.

Karickhoff *et al.* (1979) observed that sorption isotherms are linear if the concentration of hydrophobic organics in the aqueous phase is less than half of the water solubility or 10^{-5} Mol $litre^{-1}$, whichever is the lower. Above these threshold concentrations, the aqueous activity

coefficient could be affected by the solute concentration (Karickhoff, 1984). As illustrated by Table 3.1, this means that above concentrations of 1.66 mg l^{-1}, 1.32 mg l^{-1} and 0.78 mg l^{-1} for PCE, TCE and benzene respectively, sorption isotherms will begin to depart from linearality. Other workers have proposed concentrations above which sorption becomes nonlinear, these are described in the compound-group specific sections (4.3.2-4.3.8).

Influence of dissolved organic matter (DOM)

Since contaminants sorb to solid organic carbon it has been suggested that they also partition into dissolved organic matter (Larson *et al.* 1992). This could have two contrasting effects:

1. Partitioning of contaminants into more mobile DOM could increase the mobility (decrease the sorption onto aquifer material) of the contaminants;

2. The interaction of DOM with aquifer organic carbon could increase the sorptive potential of the sorbent and increase retardation.

This issue is of particular significance in landfill leachate plume investigation. It has been investigated in a number of studies as described in section 4.3.6.

Kan and Tomson (1986) used a modified retardation coefficient to take account of the sorption effects due to the presence of dissolved organic carbon at different concentrations. The results showed that retardation factors can be drastically reduced in the presence of dissolved organic carbon (e.g. humic and fulvic acids) at concentrations of 100 – 1,000 mg l^{-1}. However, others (e.g. Thornton *et al.*, 2000, Bright *et al.*, 2000) have shown higher than expected sorption in methanogenic leachate environments which was also attributed to interactions of DOM.

Competitive and Co-operative sorption

Most sorption studies reported in the literature focus on sorption parameters for a single contaminant and do not investigate the effects of the more realistic situation in which multiple contaminants are present in a plume. If estimates of sorption decrease when multiple contaminants are considered relative to a single contaminant system, then nonlinear sorption may be occurring as a result of increasingly limited availability of sorption sites or 'competitive' sorption. Evidence of this behaviour has been reported by Rivett *et al (*in submission) and Ferris (1999) – see also section 4.3.7.

In contrast, increase in sorption of contaminants has been described in the literature in multiple contaminant systems and at high concentrations of contaminants (co-operative sorption). Brusseau (1991) reported an increase in equilibrium partition coefficients in binary solute systems by a factor of 1.5 to 3 compared to single solute systems. The dual system comprised the presence of tetrachloroethene (PCE) being added to naphthalene, para-xylene and 1,4 dichlorobenzene while the single systems investigated the sorption of these three organic compounds in isolation. The enhanced sorption was postulated to result from sorbed PCE increasing the f_{oc} of the sorbent.

Desorption – non-equilibrium sorption and residence time

As mentioned in section 3, non-equilibrium sorption (i.e. assessment of the rate of sorption processes which is often described as 'rate-limited sorption') can have important implications

for sorption experiments, contaminant transport in lower permeability environments and bioavailability. Many experiments assume equilibrium conditions which may underestimate sorption processes continuing to occur after the duration of the experimental measurements.

Pignatello & Xing (1996) review the research in this area focussing on mechanisms (e.g. possible rate limiting steps, kinetic behaviour, organic matter diffusion and sorption retarded pore diffusion) and significance of slow sorption mechanism to bioavailability. Key points made by the above review include the following:

- the use of equilibrium expressions for sorption in fate and transport models is often invalid due to slow reaction kinetics. Ignoring slow kinetics can lead to an underestimation of the true extent of sorption;

- in most cases, the uptake or release of organics by natural particles is bimodal in that it occurs in fast and slow stages with a timescale of a few hours to a few days separating the 'fast' and 'slow' stages;

- the magnitude of the slow fraction can cause the apparent partition coefficient derived from a short experiment to increase by between 30% to 1000% (1 order of magnitude) while the magnitude of desorption can also increase by 10-96% following a comparatively rapid desorptive release of contaminants;

- microbes take up substrates far more readily from the fluid than sorbed states, hence, aged chemicals are resistant to degradation compared to freshly added chemicals and degradation of freshly added chemicals often tails off to leave a resistant fraction. Bioavailability can be a major limitation to complete bioremediation of contaminated soils.

In low permeability environments there is a higher likelihood of observing these effects and increased sorption may occur with time. In high permeability environments where equilibrium is unlikely to be reached, the error due to these effects is likely to be greater but the relative impact may be lower due to the importance of other factors (e.g. advective transport, biodegradation).

Key studies of non-equilibrium sorption include the following:

- Piatt & Brusseau (1998) report differences in sorption kinetics due to sorbate shape/structure and the quantity (path length) and morphology of the f_{oc};

- Roberts (1986) found that retardation factors increased by up to 150% over the duration of the 'Stanford-Waterloo' natural gradient field test at Borden. Early retardation factors were calculated after 15 days while late time data was calculated after 650 days;

- Ball & Roberts (1991b), investigating the rate of sorptive uptake of tetrachloroethene (PCE) on differing grain size material, found that the rate of approach of equilibrium was greater for smaller size fractions and for a less strongly sorbing solute (i.e. PCE approached equilibrium in the order of tens of days while 1,2,4,5 tetrachlorobenzene approached equilibriumin the order of hundreds of days).

Sorption to organic carbon or mineral matter

As described in section 3, there is a critical level of organic carbon at which the sorption of organic contaminants onto organic matter is equal to the sorption onto the mineral fraction. This critical value is often quoted as 0.001 or 0.1% although it is inversely proportional to the K_{ow} of a contaminant (see Fetter, 1999).

There are a significant number of studies conducted for sites with material below this critical f_{oc} (i.e. low f_{oc} environments). In such conditions, sorption can often be underestimated due to ignoring the effect of sorption to the mineral fraction of the aquifer. This effect works against the nonlinear effect described above in which the presence of a limited number of available sorption sites acts to reduce the amount of sorption occurring, especially at higher concentrations.

In low organic carbon environments, sorption to the mineral fraction of the aquifer becomes more important. The key mineral fraction for sorption processes is the clay minerals content. This has a positive feedback-type effect on sorption in that high clay content material usually imparts a lower permeability to the aquifer, which in turn will affect the residence time and opportunity for equilibrium sorption to occur to the f_{oc} in the aquifer.

Quantity and type of organic carbon

Quantification of the aquifer fraction of organic carbon is clearly important for the estimation of sorption parameters. The most common method is to use high temperature oxidation (HTO) followed by quantification of the carbon dioxide produced or wet chemical oxidation. Samples analysed by HTO are prepared for analysis by removing inorganic carbon using an acid followed by filtration or evaporation. A review of these methods is presented by Steventon-Barnes (2000) in which filtration is recommended for removal of inorganic carbon in high carbonate materials such as encountered within selected major UK aquifers (see section 2). Examples of overestimates in measurement of f_{oc} which compounded errors in sorption estimation are found in the literature (e.g. Benker *et al.*, 1998).

Binger *et al.* (1999) present a discussion of the influence of the type of organic carbon on sorption processes. Organic carbon originating from Devonian shales and from sediments which have undergone diagenesis exhibited much higher sorption potential (e.g. higher K_{oc}). The processes of diagenesis were shown to decrease the oxygen content and increase the aromaticity of the organic carbon leading to increased sorption potential. Surface and near-fracture weathering were shown to reduce K_{oc} values.

It follows that higher than expected sorption may occur in UK consolidated aquifers (compared to US sand and gravel systems) where organic carbon is of a reduced form and low oxygen content and/or in reducing environments.

4.3.2 Benzene, toluene, ethylbenzene and xylenes (BTEX)

BTEX compounds have low to moderate hydrophobicity and K_{ow} values (ranging from 79 – 468 l kg^{-1}, Table 3.1). Sorption of these compounds is likely to be relatively low with theoretical retardation factors presented in Table 3.1 of 2.0 – 6.6 in a low f_{oc} environment.

With the exception of a number of studies dealing with rate-limited kinetic sorption, none of the identified researchers have dealt directly with the question of the effects of contaminant concentration on the potential for sorption of BTEX compounds. Larson *et al.* (1992) touched

on the effects of concentration on sorption of BTEX by noting that linear isotherms for benzene occurred at a concentration range of 100 – 400 μg l^{-1}. This concentration range is below the empirical 10^{-5} Mol $litre^{-1}$ threshold concentration described by Karickhoff *et al.* (1979), above which, sorption was reported to depart from linearity. Concentrations resulting from application of this rule are presented in Table 3.1 and range from 0.78 – 1.06 mg l^{-1} for BTEX compounds.

Of those studies that address sorption of BTEX compounds, Thierrin *et al.* (1995) used the results of a tracer test to estimate retardation factors of 1.02 for benzene, 1.04 for toluene and 1.12 for p-xylene. These values indicate very limited sorption. The concentration range for the tests was 3-5 mg l^{-1} while the f_{oc} content ranged from 0.08-0.6%.

King *et al.* (1999) undertook a two year duration natural gradient field test of coal tar compounds (including m-xylene) at the Borden air force base. A retardation factor of 1.6 was calculated for m-xylene and a mass balance suggested that between 30 – 81g of m-xylene was sorbed to the aquifer at different time steps. This compared to a transformed mass of 227 - 347g for different time-steps.

Bright *et al.* (2000) report batch sorption experiments conducted for benzene and toluene in different clay-rich landfill liner-type environments at maximum concentrations of 385 μg l^{-1} benzene and 558 μg l^{-1} toluene. Sorption to organic carbon could not explain the experimental results and interactions of dissolved organic matter and mineral surface reactions were invoked to account for the higher than expected levels of sorption.

4.3.3 Polycyclic aromatic hydrocarbons (PAHs)

Two PAHs were included in the list of contaminants to be evaluated by this study, benzo(a)pyrene (BaP) and naphthalene (N). PAHs are hydrophobic compounds with high K_{ow} values of 1,000,000 l kg^{-1} (BaP) and 2,350 l kg^{-1} (N). Theoretical retardation factors for these compounds computed in Table 3.1 are also high ranging from 5,761 (BaP) to 15 (N).

Very little information on sorption of BaP in groundwater systems was identified by the literature search. McCarthy *et al.* (1989) found that partitioning of BaP into dissolved organic matter (which could increase BaP mobility) depended on the nature of the DOM. Specifically, DOM with open structures such as hydrophobic acids were shown to increase partitioning of BaP into DOM.

A number of studies relating to naphthalene sorption were reviewed from the literature although none deal specifically with the question of concentration effects. Lane and Loehr (1995) found that comparing batch tests with predicted sorption using published K_{oc} values were generally within an order of magnitude for PAHs, including naphthalene.

Of the other studies relating to naphthalene sorption, the following results were noted:

- Thierrin *et al* 1995. used a tracer test to estimate a retardation factor of 1.32 for naphthalene in a low f_{oc} (0.08-0.6%.) sand;

- King *et al.* (1999) calculated a retardation factor of 2.2 for the Borden aquifer. This was used in a contaminant mass balance calculation which showed that the mass sorbed (400g and 522g) for a number of time periods exceeded the mass transformed (404g and 98.3g);

- Abdul and Gibson (1986) report that adsorption of PAHs is adequately described by the linear isotherm model up to a concentration of 1 mg l^{-1} naphthalene.

It should also be noted that sorption of naphthalene can be enhanced by biological processes that covalently incorporate partially oxidised biodegradation products into soil humus (Sims & Abbott, 1992).

4.3.4 Fuel additives

Ethanol is miscible in water and will fully mix. Methyl tert-butyl ether (MTBE) is a hydrophilic compound with high solubility (relative to other petroleum components) and low K_{oc} values (Table 3.1). Sorption is not a significant attenuation process for either of these compounds (Barker *et al.*, 1996).

Garrett *et al.* (1986) reported that the presence of high concentrations of (extremely soluble) MTBE in groundwater increased the mobility (decreased the retardation) of BTEX components which were associated with a gasoline plume.

4.3.5 Phenol

In common with the fuel additives, phenol is relatively hydrophilic with a low K_{oc} value of 27 l kg^{-1} (reference Table 3.1). Given that phenol becomes negatively charged above a pH of approximately 9, sorption of phenol is pH dependent with increased cation exchange type sorption above a pH of 9. However, sorption is not likely to be an important natural attenuation process for phenol migration, especially in neutral pH range low f_{oc} environments.

King *et al.* (1999) calculated a retardation factor of 1.05 for phenol at the Borden site and used this in mass balance calculations to show that just 3g of phenol sorbed to the aquifer in the plume in comparison to 94g, which transformed after the same time-step

4.3.6 Pesticides

Very little literature has been identified which deals with the sorption of Mecoprop and Parathion in groundwater systems.

At normal groundwater pH values (5-9) Mecoprop (2-(2-methyl-4-chlorophenoxy)propionic acid) exists in the anionic form and displays little sorption (Zipper *et al.*, 1998; Williams *et al.*, 2001).

Davidson *et al.* (1980) conducted a number of experiments to estimate sorption parameters for a group of pesticides including parathion. The Freundlich model was found to adequately describe the isotherms over a wide concentration range suggesting that although sorption was nonlinear, sorption sites were not saturated at any point during the experiments.

4.3.7 Chlorinated solvents

This group of contaminants commands the greatest degree of interest from researchers in terms of volume of data available in the literature. K_{ow} values and therefore hydrophobicity tend to be low to moderate, ranging from 62 l kg^{-1} for dichloroethane to 398 l kg^{-1} for tetrachloroethene – see Table 3.1.

Retardation factors reported in the literature for the chlorinated solvent group assessed by this project generally fall within the range 1.1 – 4.0, as do the theoretical values presented by Table 3.1 (although retardation factors as high as 9.0 have been reported). Most identified literature presents the results of overseas laboratory or field experiments often from pure sand and gravel environments which are low in aquifer f_{oc} content.

Effects of Contaminant Concentration

A small number of researches have dealt with the specific question of the effect of contaminant concentration on the potential for sorption of chlorinated solvents. Ball & Roberts (1991a) studied the sorption of PCE using batch experiments with aquifer materials from the Borden Air Force Base, Ontario. A PCE concentration range for the study of 4-5 orders of magnitude was used for the experiments. At concentrations of less than 100 μg l^{-1}, the experimental data fitted linear sorption isotherms well. Departure from linearity occurred at approximately 1,000 μg l^{-1}, above which use of a linear model resulted in overestimation of the amount of sorption. The data were found to fit a nonlinear Freundlich isotherm with a Freundlich exponent of 0.8. Rao and Davidson (1980) reported that for a solution concentration of 10 mg l^{-1} (of hydrophobic organic contaminant) and a Freundlich exponent of 0.7, the amount sorbed could be overestimated by a factor of two.

The Ball & Roberts (1991a) study also found that at lower concentrations K_d values were higher than expected. This was assigned to the longer timescales of the experiments and the role of mineral phase sorption. Indeed, the role of mineral phase sorption (as often reported in low f_{oc} environments) was linked to the nonlinearity of the isotherms. A mechanism of physical adsorption to heterogeneous sites was put forward as a key reason for the nonlinearity observed. Physical adsorption to heterogeneous sites is a process best described by the concentration-dependent Freundlich isotherm model (Weber *et al.*, 1992, Allen-King *et al*, 1996).
Piwoni and Banerjee (1989) designed similar experiments to investigate sorption isotherms for a range of chlorinated solvents in sands with moderate clay content (6-23%) and low f_{oc}

content (<0.1%). They found that sorption isotherms for PCE were linear up to a concentration of 2,000 μg l^{-1}, above which the isotherm departs from the linear model and over-estimation of sorption would occur if the linear model had been used at higher concentrations. Again, higher-than-expected sorption occurred in the results at lower concentrations, this was attributed to mineral-phase sorption.

Allen-King *et al.*, 1996, investigated the sorption of PCE to four natural clay-rich aquitards over a wide PCE concentration range (1 – 90,000 μg l^{-1}). Linear isotherms were found to underestimate sorption effects at lower concentrations and overestimate sorption in high concentrations. In one of the aquitards studied (f_{oc} = 0.5% or 0.005), the retardation factor (defined as bulk density x K_d / porosity) varied from 60 at a concentration of 1 μg l^{-1} to just 3 at 60% PCE solubility.

Rivett *et al* (in submission) reported the results of a natural gradient free-phase emplaced source (ES) tracer test in Borden, Ontario. Concentrations resulting from this experiment ranged from 1 μg l^{-1} to 100,000 μgl^{-1} (n.b. very little research has addressed the issues associated with sorption at such high concentrations) while comparison of tetrachloroethene (PCE) sorption behaviour with an earlier 'Stanford-Waterloo (SW)' natural gradient tracer test was possible. Key findings of this research included the following:

- although 3-D numerical simulations assuming linear sorption achieved a reasonable fit, single and multi-solute laboratory studies indicated nonlinear sorption isotherms and competitive sorption effects;

- the magnitude of the retardation was three times less than the final value reported by the previous test (the Roberts 1986 study showed an increase in the retardation factor for PCE from 2.7 to 5.9 with travel time and distance). Possible explanations include:

    - the nature of the f_{oc} which was considered by the authors likely to be a contributing factor to differences in results between the two test sites even though they are located only 150m apart. The ES site appeared less sorbing, suggesting that the f_{oc} at the ES site consists of more oxidised carbonaceous matter, which was consistent with qualitative filed observation;

    - the effect of competitive solutes: comparison of PCE only and PCE and TCE isotherms indicated a decreased sorption of the latter over the entire concentration range tested that is indicative of competition from the, albeit weakly sorbing, TCE solute;

    - single solute concentration isotherm differences showed that retardation magnitude in the SW test was twice that of the ES test at low concentrations indicating differences in sorbate material rather than concentration effects. However, the degree of nonlinearity was reported with Freundlich n exponents quoted as 0.92 (ES) and 0.81 (SW) for the high concentration range. This resulted in two or three times less retardation at higher concentrations (retardation factors for PCE dropping from 2.6-3.4 to 1.8-3.2 (ES) and 4.7-6.3 to 1.6-6.8) which can be attributed to nonlinear Freundlich sorption behaviour over large solute concentration ranges.

- Both tests exhibited evidence of non equilibrium sorption although this behaviour was more obvious in the SW test which showed a gradual increase in retardation with time.

Shepherd *et al.*, 2001 present interim results of an ongoing investigative programme which is addressing the spatial variability of sorption in the Birmingham aquifer, UK. PCE sorption has been shown to fit a nonlinear model with Freundlich partition coefficients ranging from 0.17 – 1.32 and retardation factors from 1.7 – 9.0. Most samples showed a two-fold reduction in the retardation factor (derived in this case from the Freundlich distribution coefficient, K_f) as the experiment concentration increased from 1 μgl to 1 mg/l. Sorption was reported to vary heterogeneously between separate sandstone and mudstone lithologies.

Collated nonlinear sorption parameters are summarised in Table 4.17 below:

Table 4.17 Collated nonlinear sorption parameters

Researchers	Freundlich exponent (n)	K_f	Contaminant Concentration range
Ball & Roberts (1991a)	0.79 – 0.95	0.72 – 2.3	<50 μg l^{-1} – 50 mg l^{-1}
Rivett *et al* (in submission)	0.89 – 0.95	0.33 – 0.50	1 μg l^{-1} – 100 mg l^{-1} or effective solubility
Shepherd *et al* 2001	0.75 – 1.07	0.17 – 1.32	1 μg l^{-1} and 1 mg l^{-1}

Although nonlinearity has been observed in these studies and in selected cases threshold concentrations have been quoted, it is considered that there is not currently a sufficient dataset to derive robust minimum/maximum concentrations at which linear or nonlinear sorption behaviour is occurring.

Effect of Mineral Fraction

Many researchers have reported that in low f_{oc} environments mineral sorption of low Kow dissolved contaminants becomes important (e.g., Ball & Roberts (1991a) Piwoni and Banerjee (1989) and Thornton *et al.*, 2000). Benker *et al.* (1998) present a study that contrasts with this general view by proposing that even in low f_{oc} environments organic-carbon based correlation may be appropriate for sorption estimation, however, this study also reported inaccurate f_{oc} content determination. Thornton *et al.* (2000), investigating sorption of chlorinated solvents in UK sandstone rocks supported the commonly held view of additional sorption to clay minerals at low f_{oc}. McKay and Trudell, 1989 note that the carbon-referenced sorption model may only be appropriate for contaminants with K_{ow} values greater than 1,000 l kg^{-1} (see also section 4.3.1).

Influence of dissolved organic matter (DOM)

Larson *et al.* (1992) investigated the effects of landfill leachate on sorption of chlorinated hydrocarbons for a number of different aquifer materials. As has been described in section 4.3.1, either increased or decreased sorption can occur as a result of the presence of DOM. This study found that distribution factors either increased or decreased by a factor of not more than two as a result of the presence of the dissolved organic carbon. Thornton *et al.* (2000), while investigating sorption and degradation of migrating acetogenic and methanogenic landfill leachates in UK Triassic sandstones found:

- Lower than expected retardation in acetogenic phase leachate (high in natural dissolved organics such as fatty acids) possibly due to colsolvency effects where two sorbents (the aquifer f_{oc} and the DOM) are competing for the same sorbate (the chlorinated solvents);

- Higher than expected retardation in methanogenic leachate possibly due to interactions with DOM (including negatively charged humic acids) which can preferentially sorb to aquifer mineral content.

Other sorption studies of chlorinated solvents

Bright *et al.* (2000) investigated the sorption of selected chlorinated solvents for two UK landfill liner materials with differing clay and organic carbon content in laboratory columns. Conclusions were as follows:

- increased sorption was observed with increasing f_{oc} to an extent that could not be explained by the increase in f_{oc} alone;

- possible reasons for the higher than expected sorption were put forward including interaction with leachate colloidal or dissolved organic matter and/or the relative affinity of clay liner f_{oc} to organic contaminants;

- evidence of increased sorption for slower flow rate experiments was identified suggesting that non-equilibrium sorption was taking place in these low permeability clay liner materials.

Odutola *et al.* (2000) used kinetic and equilibrium batch sorption experiments to evaluate the significance of sorption of chloroform in low f_{oc} content karstified limestone. Although chloroform is not one of the contaminants included in this project, it is included here due to the rarity of studies estimating the sorption parameters in fractured limestone environments. A key finding of the study was that use of organic carbon-based linear sorption would have underestimated the sorption potential of the limestone (K_d=0.01 using f_{oc} assumption, K_d up to 0.096 using a Freundlich isotherm).

Two column studies using material from the Carboniferous sandstone in Coventry, UK by Mouvet *et al.* and Bourg *et al.* (both 1993) present a relatively 'ideal' view of sorption in the particular environments studied (sandstone, f_{oc}=0.2% and various unconsolidated deposits). Retardation factors for the Coventry sandstone were similar to the theoretical values presented in Table 3.1, (TCA<2, TCE<3 and PCE<4). Sorption isotherms were reported to be linear in the concentration range studied of up to 1,000 $\mu g\ l^{-1}$ with sorption related to the f_{oc} content and some evidence of non-equilibrium sorption.

Curtis *et al.* (1986) present a further example of linear sorption at low concentration ranges for PCE at the Borden test site in Ontario (pure sand, low f_{oc}). This study attributed slightly higher than expected K_d values to additional sorption to mineral surfaces.

4.3.8 Cyanides

The fate of cyanides in groundwater is complex because cyanides have the potential to undergo a wide variety of reactions in the subsurface (Figure 4.18). In most cases sorption is not a significant attenuation mechanism due to the high solubility of the complex ions in the aqueous environment.

4.4 Summary of Sorption Literature

The following tables summarise the key issues reviewed in the literature relating to sorption.

Table 4.18 Sorption Literature Summary : Contaminant concentration effects

Reference	Contaminant	Summary
Karickhoff *et al*, 1979	'hydrophobic organic compounds'	sorption isotherms are linear if the contaminant concentration is less than half of the solubility or 10^{-5} M l^{-1}, whichever is the lower (see also Table 3.1)
Larson *et al*, 1992	benzene	Linear sorption behaviour within a concentration range of 100 – 400 μg l^{-1}
Abdul & Gibson (1986)	naphthalene	Linear sorption behaviour below a concentration of 1,000 μg l^{-1}
Ball & Roberts (1991a)	PCE	Linear sorption behaviour below a concentration of 1,000 μg l^{-1}
Piwoni & Banerjee (1989)	PCE	Linear sorption behaviour below a concentration of 1,000 μg l^{-1}
Bourg *et al*, 1993 and Mouvet *et al,*1993	TCA, TCE, PCE	Linear sorption behaviour below a concentration of 1,000 μg l^{-1}
Allen-King *et al,*1996	PCE	Up to 20-fold variation in retardation factor for Freundlich sorption to aquitards over full concentration range (1 – 90,000 mg l^{-1}) for the most nonlinear isotherm (Freundlich n=0.72)
Odutola *et al,*2000	Chloroform (included due to general lack of fractured aquifer sorption studies)	linear sorption would have underestimated the sorption potential of the limestone by one order of magnitude
Rivett *et al*, in submission	PCE	Retardation factors were two to three times lower at high concentrations although the degree of nonlinearity was less than other studies (in this case Freundlich n=0.92)
Shepherd *et al*, 2001		Retardation factors were generally half the value at high concentrations. The degree of nonlinearity was variable with Freundlich n ranging from 0.75 – 1.07

Table 4.19 Sorption Literature Summary : Influence of co-contaminants

Reference	Contaminant	Summary
Thornton *et al,* 2000	Chlorinated solvents, BTEX and dissolved organic matter from M type and A type landfill leachate	Lower than expected retardation in acetogenic phase leachate (high in natural dissolved organics such as fatty acids) possibly due to two sorbents (the aquifer foc and the DOM) competing for the same sorbate (the chlorinated solvents); Higher than expected retardation in methanogenic leachate possibly due to interactions with DOM (including negatively charged humic acids) which can preferentially sorb to aquifer mineral content (i.e. clay minerals).
Rivett *et al,* in submission	PCE, TCA	comparison of PCE only and PCE and TCE isotherms indicated a decreased sorption of the latter over the entire concentration range competition from TCE
Brusseau, 1991	PCE, naphthalene, xylene	Increased sorption due to co-solvent effects

These data indicate that there does not appear to be a single set of rules that govern the sorption of hydrophobic organic compounds at different concentrations. The following general points are made:

- Linear sorption can be adequate at low concentrations to quantify sorption;

- When considering a range of concentrations and heterogeneous sorption environments, nonlinear Freundlich sorption behaviour is likely to provide a better means of quantification, although in some cases, the linear model can provide a reasonable approximation over a range of concentrations. At higher contaminant concentrations, less sorption than predicted by the linear model is likely but this is not always the case;

- Other effects that could lead to errors of up to two orders of magnitude (typically these effects may lead to errors in retardation factors by a factor of 2 or 3) include:

    - cosolvency effects,
    - non-equilibrium sorption,
    - sorption to aquifer mineral content (when it has been assumed all sorption takes place within aquifer f_{oc});
    - nature of aquifer f_{oc}.

5. CONCLUSIONS

5.1 Data Quality

A number of important natural attenuation processes are contaminant concentration dependent. These are:

- diffusion;
- sorption (including non-equilibrium sorption which is effectively a diffusion-controlled processes);
- volatilisation;
- chemical (abiotic) degradation;
- biodegradation.

At the outset of this project, it was expected that a sizeable body of literature addressed contaminant fate in the subsurface including details of the effects of contaminant concentrations on natural attenuation processes. The outcome of the literature review indicated that the body of useful literature is currently smaller than might reasonably be expected. Research papers reviewed exhibited the following problems:

- a significant proportion of papers reviewed do not describe contaminant concentration or provide sufficient detail to allow it to be estimated reliably;
- a significant proportion of papers reviewed fail to provide sufficient data on ambient conditions to allow for extrapolation;
- many individual references actually provide the same data for the same site.

Of those papers that do provide sufficient information, the great majority relate to sand-gravel aquifer systems and are almost entirely from outside the UK.

5.2 Translation of Research Data from to UK environments

The translation of literature data (e.g. US Research sites) to estimate rates in important UK aquifers is problematic. For consolidated aquifer systems, particularly the fractured sandstone and chalk systems that represent the major UK aquifers, there are almost no data for the contaminants reviewed in this report and very few relevant data of any kind that could guide an estimation process. Where there are no supporting datasets, any indication of potential rates is no better than guesswork and we have therefore made clear in the contaminant summary (Section 4.2) where insufficient data exist. Site-specific data will be invaluable for these cases.

For many shallow sand-gravel aquifers, wide variation of degradation rates for a contaminant was identified in the literature for this type of aquifer. Possible explanations for these variations include:

- differences in temperature which can be corrected by the Arrhenius equation for chemical processes or the Q_{10} concept for biological ones (Appendix 3);
- variation in hydrogeological conditions such as flow velocity;

- mineralogical differences between different sand and gravel aquifers;
- different types of microbial communities;
- differences in data interpretation, sampling procedures, etc.

Hence, degradation rates reported in the literature for a specific contaminant and environment (e.g. aerobic benzene degradation in a shallow sand and gravel aquifer) can only be used as a guide to the likely degradation rate at another site with similar conditions.

5.3 The Effects of Contaminant Concentration on Natural Attenuation

Reliable estimates of contaminant attenuation rates for many contaminants under specific biogeochemical and hydrogeological conditions have been identified by this project. In addition, an "active microbial range" or threshold concentration has been defined for contaminants (see tables in Section 4.2) outside which rates dramatically decrease. However, it has proved extremely difficult to derive relationships between contaminant concentration and rate. Concentration effects are usually difficult to discern from the background noise generated by the other variables in laboratory and field measurements, such as:

- physical aquifer properties such as porosity and hydraulic conductivity;
- aquifer geochemistry, including clay, organic carbon, iron and manganese contents and clay and organic carbon structure;
- aquifer hydrochemistry, including redox potential, dissolved oxygen and other respiratory substrates;
- contaminant mixtures, which may enhance or inhibit attenuation of the contaminant under consideration;
- microbial activity, which is likely to vary and decrease with increasing aquifer depth;
- contaminant-specific characteristics (e.g., degradation pathways, hydrophobicity);
- differences in sampling and data interpretation;
- differences in laboratory experimental design.

Furthermore, those processes that are, in part, dependent on contaminant concentration, often interact with each other under the influence of site-specific conditions, for example:

- interactions between individual chlorinated solvents and interactions between BTEX and fuel additives can inhibit or enhance biodegradation rates, dependent on the relative concentrations of the components;
- sorption can remove contaminants from solution and reduce their availability for biodegradation;
- conversely, at low contaminant concentrations, sorption may enhance biodegradation rate by making contamination more available to surface-attached microorganisms.
- sorption can be rate-limited by diffusion within a particle or organic matter in an aquifer;
- multiple contaminants can increase or decrease sorption and dissolution.

For the above reasons, a clear generic relationship between concentration and attenuation process rate cannot be established, even though it exists theoretically and can be demonstrated in specific and well-controlled studies performed at a single site.

5.4 Sorption

The potential for sorption of contaminants assessed for this project generally depends upon aquifer organic carbon content, contaminant hydrophobicity and contaminant concentration. The contaminants assessed divide into three groups when assessing sorption processes:

1. Benzo(a)pyrene is extremely hydrophobic and possesses very low water solubility and therefore sorption may be a powerful enough process to prevent it migrating through the unsaturated zone to an aquifer. If it does reach groundwater, sorption may be an important attenuation process.

2. BTEX compounds, chlorinated solvents, naphthalene and parathion are grouped here in a category within which sorption may be either of primary or secondary importance to a natural attenuation assessment especially with increasing aquifer f_{oc} content. There is evidence from the literature that above chlorinated solvent concentrations of 1-2 mg l^{-1}, a linear sorption model will increasingly overestimate the degree of sorption.

3. Phenol, ethanol, Mecoprop, parathion and MTBE are unlikely sorb to any significant degree regardless of contaminant concentration.

In summary, the following conclusions have been drawn in respect to sorption processes:

- Linear sorption can be adequate at low concentrations to quantify sorption;

- When considering a wide range of concentrations in heterogeneous sorption environments, nonlinear, Freundlich sorption behaviour, in which retardation magnitude varies with contaminant concentration, is likely to provide a better means of quantification. Variation in the magnitude of retardation at different concentrations can range from a factor of 2-3 up to, in one case, a factor of 20. At higher contaminant concentrations, less sorption than predicted by the linear model is likely although in some cases the linear model can provide a reasonable approximation over a range of concentrations;

- Other effects that could lead to errors of up to two orders of magnitude (typically these effects may lead to errors in retardation factors by a factor of 2 or 3) include:

    - cosolvency effects,
    - non-equilibrium sorption,
    - sorption to aquifer mineral content (if it has been assumed all sorption takes place within aquifer f_{oc});
    - nature and composition of aquifer f_{oc}.

5.5 The role of generic attenuation rate data in MNA evaluation

Compiled data and derived general ranges of attenuation rates, such as those compiled in this report, should be considered as no more than indications of the potential for MNA. Attenuation rates are highly sensitive to conditions in the field, which may vary seasonally, in different parts of the plume and for other site-specific reasons. For the UK, the uncertainty is compounded by the lack of a significant dataset on attenuation rates in aquifers. For these reasons, Environment Agency R&D Report 95 (Environment Agency, 2000a) emphasises the importance of "lines of evidence" for MNA established using site data gathered in the field over a reasonable period.

Experience and data from comparable sites can play a beneficial role in assessment of MNA, particularly in the early stages of evaluation where only limited site data may be available and also in cross-checking that site estimates of attenuation rates are reasonable.

The generation of "lines of evidence" should be based primarily on field-measured data and often field data alone will be fully satisfactory (Environment Agency, 2000a). It is important to note that laboratory measured data for concentration-dependent natural attenuation processes usually significantly overestimate the rate in the field, often by an order of magnitude or more, leading to major errors when laboratory data are applied uncritically to the evaluation of field processes

5.6 Identification of knowledge gaps and research needs

This project has demonstrated that most of the reported information on contaminant fate in groundwater has been generated for aquifers outside of the UK and cannot readily be translated to the Major Aquifers of the UK, particularly the fractured sandstone and chalk. This highlights that the following research areas should be encouraged to provide relevant data on key MNA processes relevant to the UK:

- Further investigation of UK fractured aquifer systems, particularly the chalk and sandstone, to determine ranges of attenuation rates under fracture flow conditions and microbial degradation activity.
- Model simulations and associated sensitivity analysis for specific contaminants, under defined sets of conditions relevant to major UK aquifers, to determine to what extent NA processes (both individual and combined) of sorption, diffusion and degradation are a significant cause of contaminant attenuation. The results of such an assessment could be used as an initial indication of the relevant importance of different natural attenuation processes for specific contaminants and defined groups of site conditions.
- The bioavailable concentrations of iron and manganese in UK aquifers and their importance to microbial respiration.
- Natural attenuation demonstration projects, including learning from cases where MNA is not effective.

The importance of such research being undertaken by appropriate multidisciplinary teams is emphasised to ensure that the generated data are relevant and applicable.

On a more fundamental level, a number of key gaps can be identified in the research reviewed in this report, in particular:

- Further investigation of UK fractured aquifer systems to determine the distribution and extent of microbial activity *in situ*.
- Further investigation into biodegradation at high concentrations close to NAPL sources, in particular whether this can have a significant effect on source longevity.
- Further investigation into biodegradation at very low substrate concentrations for those contaminants that may pose a significant risk at such concentrations.
- Investigation of sorption effects at high contaminant concentrations.
- Vadose zone natural attenuation.

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GLOSSARY

Abiotic	Reaction that takes place without the involvement of biological activity.
Adsorption	The attachment of a chemical to the surface of a solid or liquid
Aerobic	Biological activity utilising oxygen as the respiratory substrate
Anaerobic	Biological activity using substrates other than oxygen as respiratory substrates.
Bioavailability	*In situ* availability of a chemical to biological processes
Biodegradation	Biological conversion of a contaminant into simpler compounds
Biofilm	Layer of microorganisms embedded in a polysaccharide layer attached to a solid surface
BTEX	Benzene, toluene, ethylbenzene and xylenes
Carbon and energy source	Organic compound that serves as source of carbon for cell growth and an electron donor (q.v.) to the respiratory chain.
Chiral	A compound whose molecular structure, otherwise identical, can exist in two or more distinct three-dimensional spatial forms.
Co-metabolism	Fortuitous metabolism of a compound by microorganisms metabolising other compounds. The microorganisms gain no benefit from the co-metabolism.
DCA	Dichloroethane
DCE	Dichloroethene
Dehalorespiration	Utilisation of chlorinated solvents and chlorinated aromatics as respiratory substrates under anaerobic conditions.
Denitrification	Anaerobic biological activity utilising nitrate as electron acceptor. The end-product of respiration is usually N_2 but intermediate formation of nitrite or nitrous oxide may be detected.
Electron donor	Substrate that is used in metabolism to supply electrons to the respiratory chain and is hence oxidised. For the microorganisms described in this report, the electron donor is normally an organic compound that serves as a carbon and energy source (q.v.).

Elimination	Chemical reaction involving an internal rearrangement of an organic molecule. An example is the reaction of 1,1,1-trichloroethane to yield 1, 1-dichloroethene: $CH_3CCl_3 \rightarrow CCl_2CH_2 + H^+ + Cl^-$
Enantiomers	Spatially distinct molecular structures of a chiral (q.v.) compound.
f_{oc}	Fraction of aquifer organic carbon
Gasoline	Petrol
H	Henry's law constant
Hydrolysis	This is a reaction between an organic contaminant and water. An example is that of 1,1,1-trichloroethane to yield acetic acid: $CH_3CCl_3 + 2H_2O \rightarrow CH_3COOH + 3H^+ + 3Cl^-$
Hydrophobic compounds	These compounds can be dissolved in many nonpolar solvents but have limited a low solubility in water due to their nonpolar nature relative to water. The lower their polarity, relative to water the higher the compounds' hydrophobicity.
Iron-reduction	Anaerobic biological activity utilising iron (III) as an electron acceptor. The product of respiration is iron (II).
K_d	In a heterogeneous system of two or more phases in equilibrium, the ratio of the activities (or less accurately the concentrations) of the same molecular species in the phases is a constant at constant temperature. This constant is termed the partition coefficient.
K_{oc}	the partition coefficient for organic carbon is defined as K_d normalised to the aquifer matrix f_{oc}
K_{ow}	the octanol-water partition coefficient is a measure of the hydrophobicity of a compound and is expressed as the ratio of the concentration of a contaminant in *n*-octanol to water at equilibrium under defined test conditions
Manganese-reduction	Anaerobic biological activity utilising manganese (IV) as an electron acceptor. The product of respiration is manganese (II).
Methanogenesis	Anaerobic biological activity generating methane as the end-product of respiration.
Mineralisation	Biodegradation that leads to the transformation of contaminants into inorganic end-products, such as carbon dioxide, water, methane, chloride ions, etc.
MNA	Monitored natural attenuation
MTBE	Methyl *tert*-butyl ether

m-xylene	1,3-dimethylbenzene
NA	Natural attenuation
NAPL	Non-aqueous phase liquid
Oligotrophic	Environment that contains extremely low concentrations of nutrients. Microbial activity under such conditions.
Oxidation-reduction	Any reaction which involves the transfer of one or more electrons between chemicals. Microbial respiration is a series of redox reactions. Certain organic chemicals may be abiotically degraded by oxidation-reduction reactions under groundwater conditions; an example is the reduction of carbon tetrachloride (tetrachloromethane) to yield chloroform (trichloromethane): $CCl_4 + H^+ + 2e^- \rightarrow CHCl_3 + Cl^-$
o-xylene	1,2-dimethylbenzene
PAH	Polycyclic aromatic hydrocarbon
PCE	Tetrachloroethene (perchloroethylene)
p-xylene	1,4-dimethylbenzene
Redox	See oxidation-reduction
Reductive dechlorination	Anaerobic co-metabolic biodegradation of chlorinated contaminants involving stepwise removal of chlorine atoms from the chlorinated contaminant molecule and their replacement by hydrogen.
S_{ind}	Substrate concentration below which metabolism of a compound is not induced (S_{ind})
S_{min}	Substrate concentration below which metabolism of a compound cannot continue (S_{min})
Sulphate-reduction	Anaerobic biological activity utilising sulphate as an electron acceptor. The product of respiration is sulphide, which will normally be detected in groundwater as H_2S or metal sulphide salts.
TCA	Trichloroethane
TCE	Trichloroethene
Terminal electron acceptor	Substrate that is reduced in the final stage of respiration. Common electron acceptors used by microorganisms include oxygen, nitrate, iron (III), sulphate and CO_2.
VC	Vinyl chloride

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Martyn Lambson (BP Amoco)
Geoff Williams (BGS)

APPENDICES

APPENDIX 1

LIST OF FIGURES

Figure 3.1: Characteristic Adsorption Isotherm Shapes

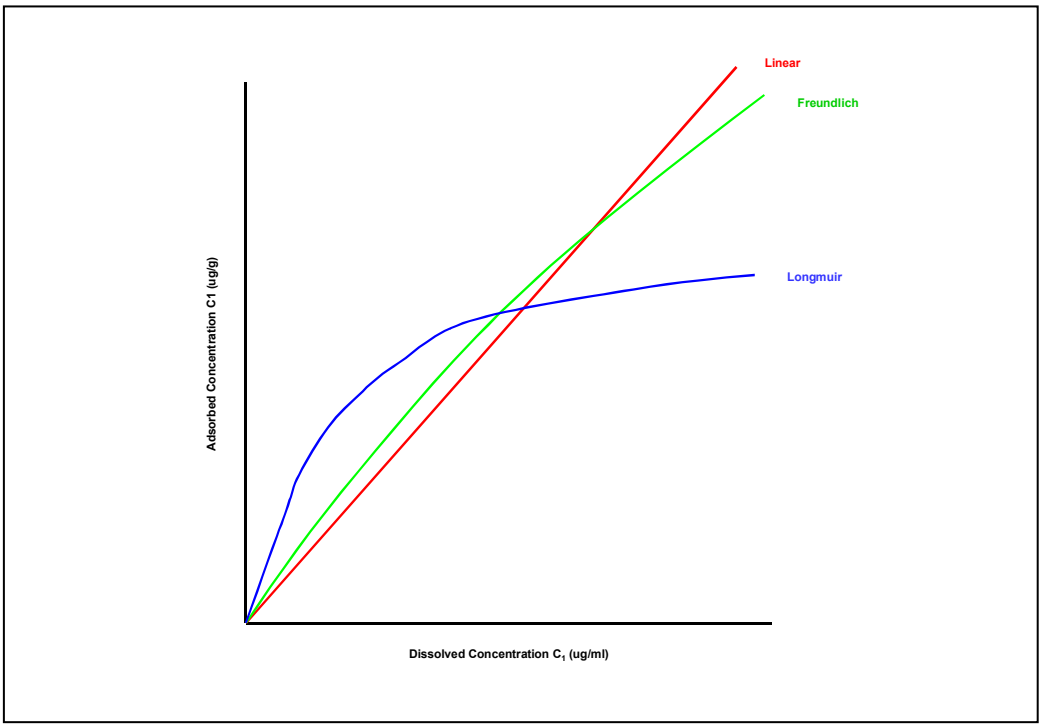


Figure 3.2: Schematic representation of aerobic microbial metabolism

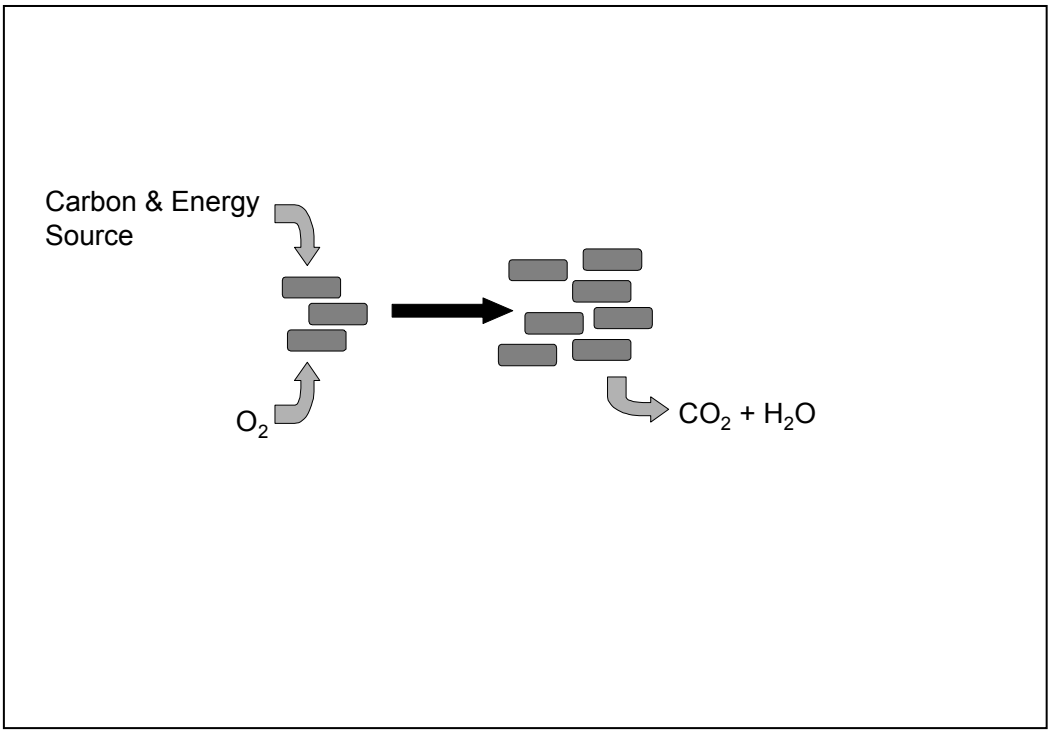


Figure 3.3: Schematic representation of anaerobic microbial metabolis

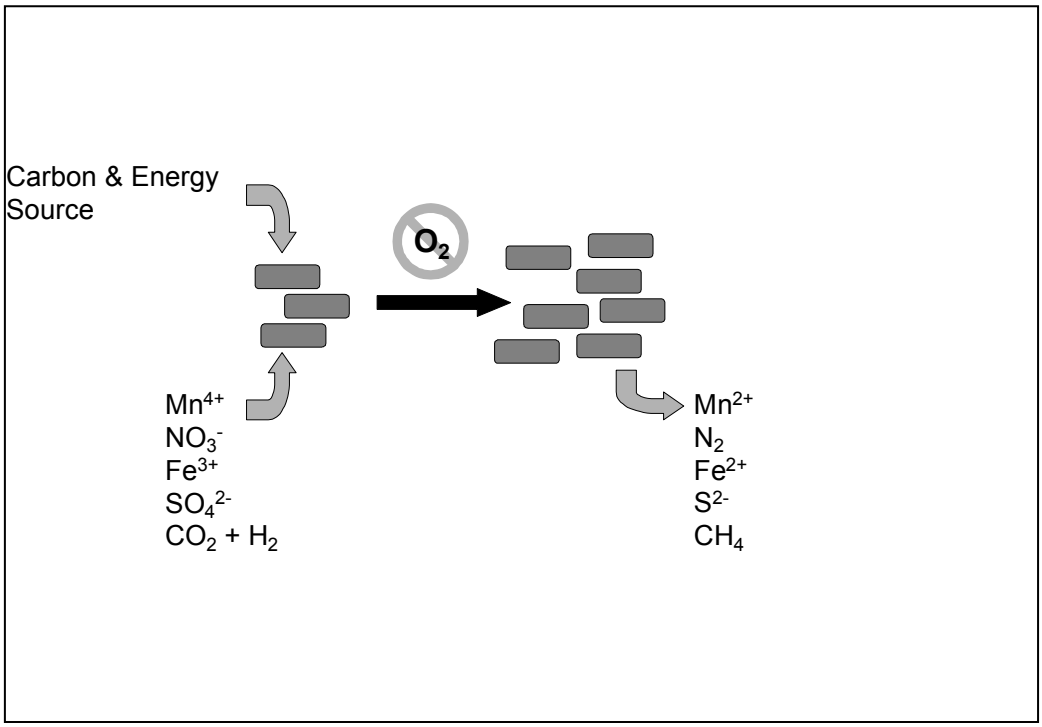


Figure 3.4: Schematic epresentation of reductive dechlorination of chlorinated solvents

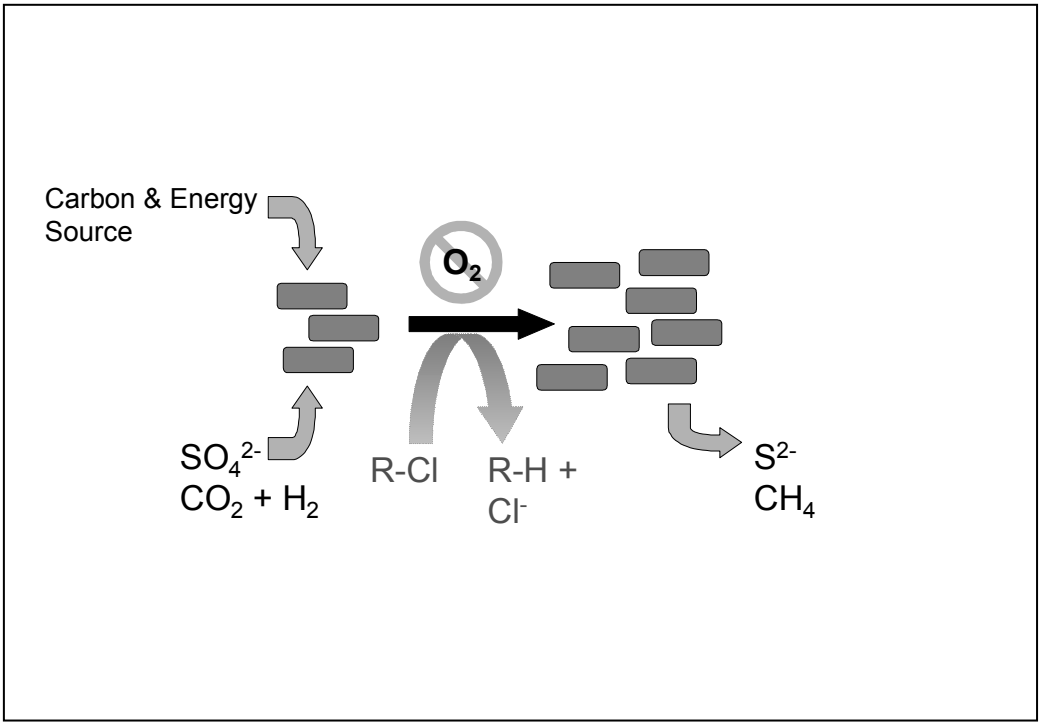


Figure 3.5 : Schematic representation of dehalorespiration of chlorinated solvents

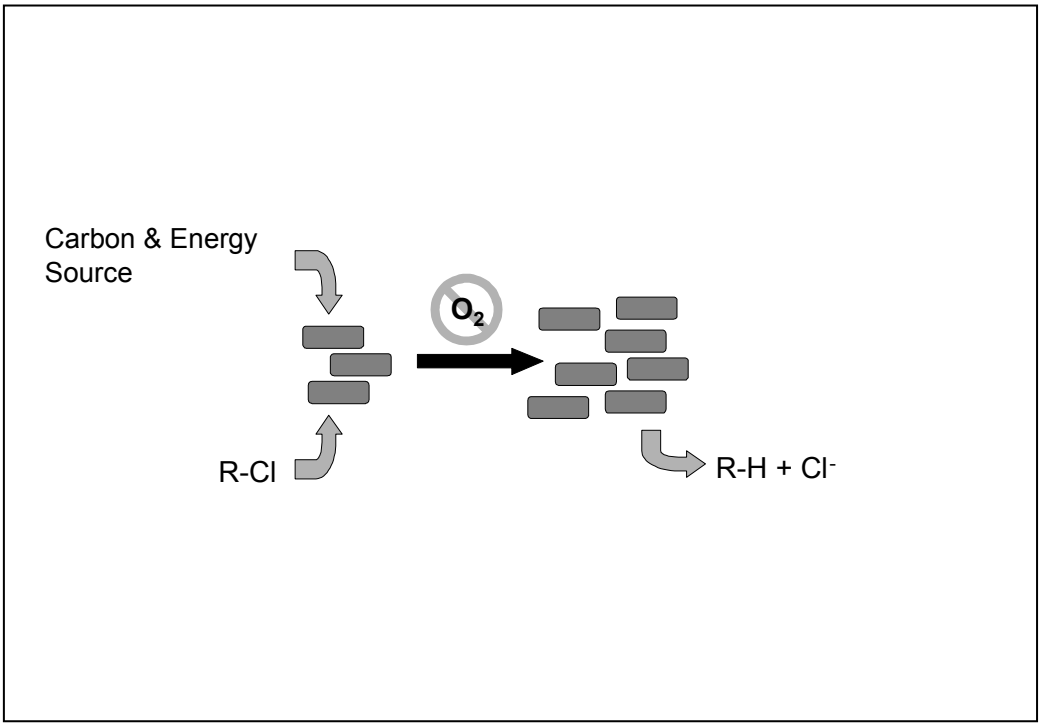


Figure 3.6: Conceptual illustration of the effect of contaminant concentration on biodegradation rate

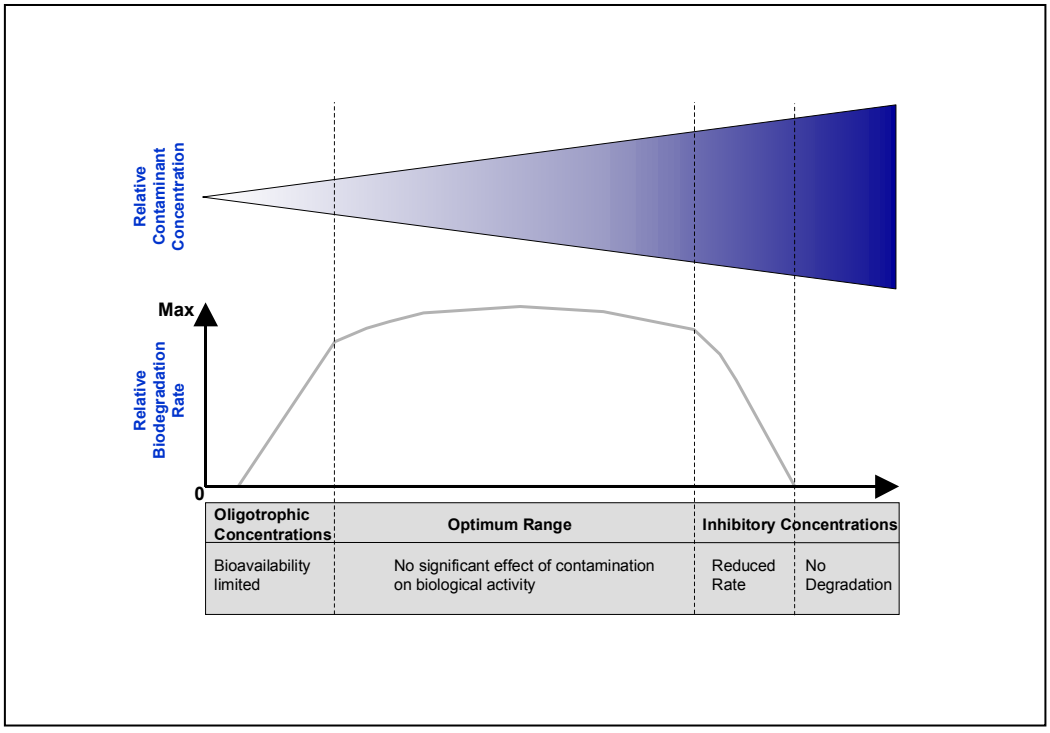


Figure 4.1: Summary of aerobic biodegradation rates of BTEX in laboratory and field studies. Shaded bars = lab; open bars = field. Data from Suarez & Rifai (1999).

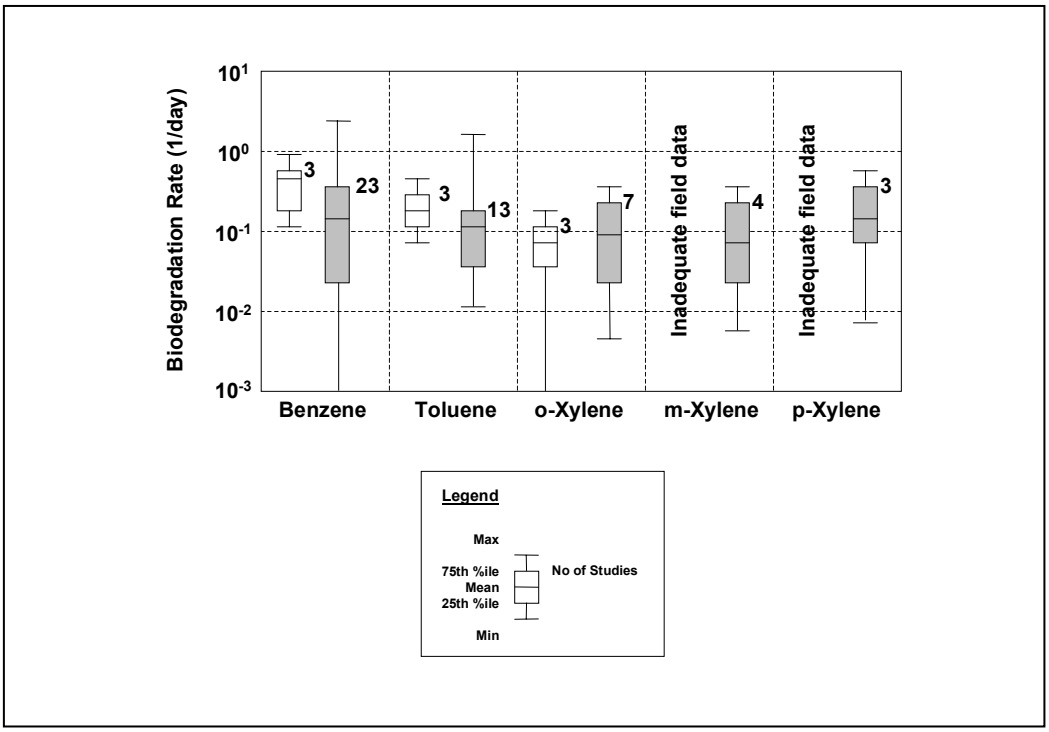


Figure 4.2: Summary of anaerobic biodegradation rates of BTEX in laboratory and field Studies. Shaded bars = lab; open bars = field. Data from Suarez & Rifai (1999).

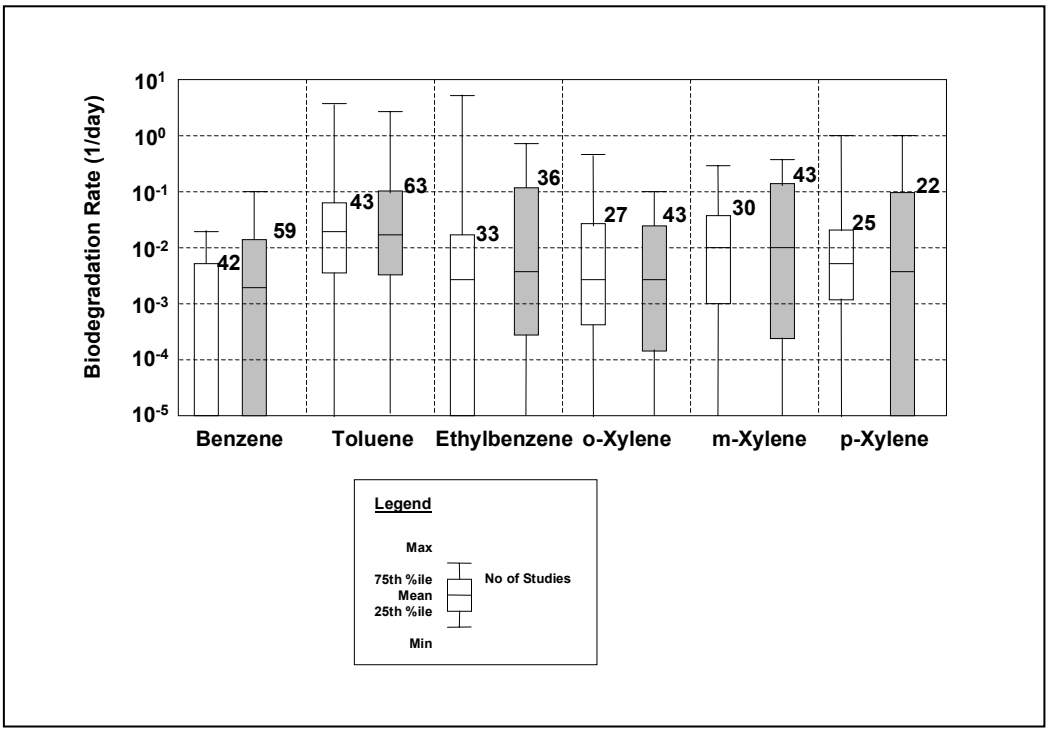


Figure 4.3: Rate of anaerobic benzene biodegradation as a function of initial contaminant concentration derived from the data compiled by Arenson & Howard (1997). Experimental data reported by Arenson & Howard that included both contaminant concentration and a biodegradation rate were selected for this graph. For those datasets reporting a range of values, only the lowest were taken; for rate data designated as less or more than a specified rate, the value for plotting was taken to be equivalent to the stated rate. No distinction was made between experiment type or temperature.

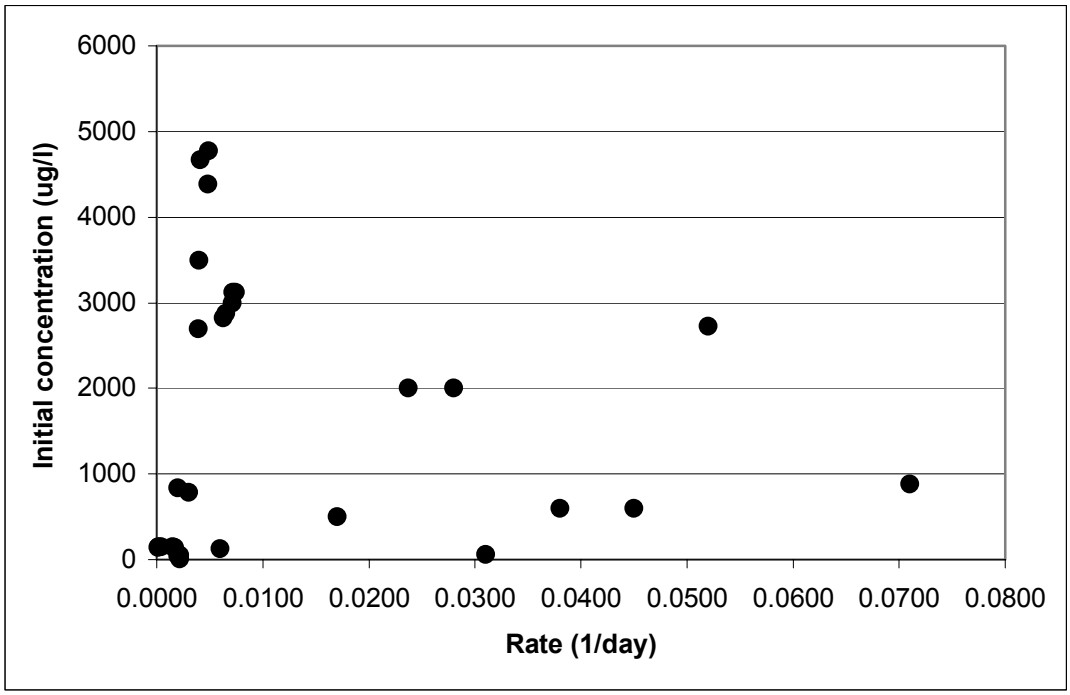


Figure 4.4: Rate of anaerobic toluene biodegradation as a function of initial contaminant concentration derived from the data compiled by Arenson & Howard (1997). Experimental data reported by Arenson & Howard that included both contaminant concentration and a biodegradation rate were selected for this graph. For those datasets reporting a range of values, only the lowest were taken; for rate data designated as less or more than a specified rate, the value for plotting was taken to be equivalent to the stated rate. No distinction was made between experiment type or temperature.

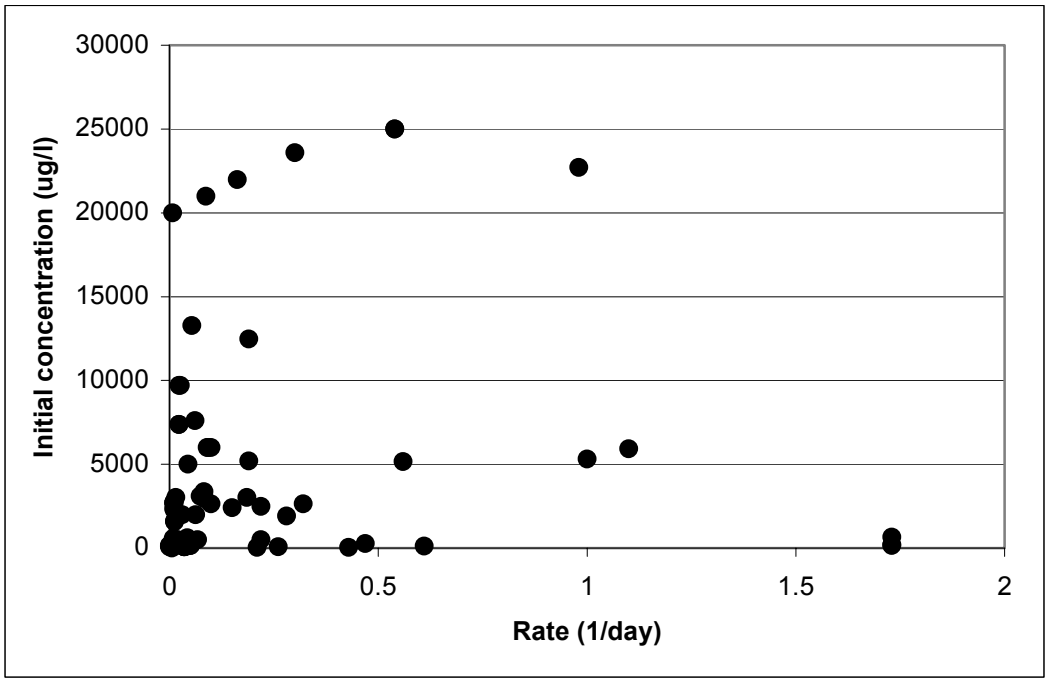


Figure 4.5: Rate of anaerobic ethylbenzene biodegradation as a function of initial contaminant concentration derived from the data compiled by Arenson & Howard (1997). Experimental data reported by Arenson & Howard that included both contaminant concentration and a biodegradation rate were selected for this graph. For those datasets reporting a range of values, only the lowest were taken; for rate data designated as less or more than a specified rate, the value for plotting was taken to be equivalent to the stated rate. No distinction was made between experiment type or temperature.

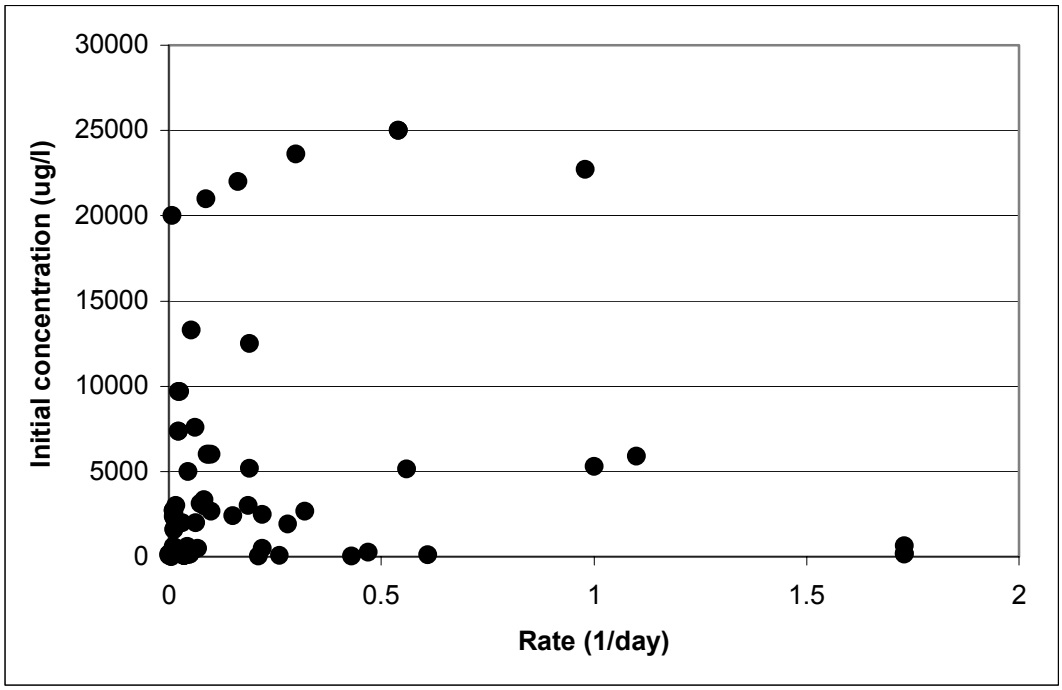


Figure 4.6: Rate of anaerobic *o*-xylene biodegradation as a function of initial contaminant concentration derived from the data compiled by Arenson & Howard (1997). Experimental data reported by Arenson & Howard that included both contaminant concentration and a biodegradation rate were selected for this graph. For those datasets reporting a range of values, only the lowest were taken; for rate data designated as less or more than a specified rate, the value for plotting was taken to be equivalent to the stated rate. No distinction was made between experiment type or temperature.

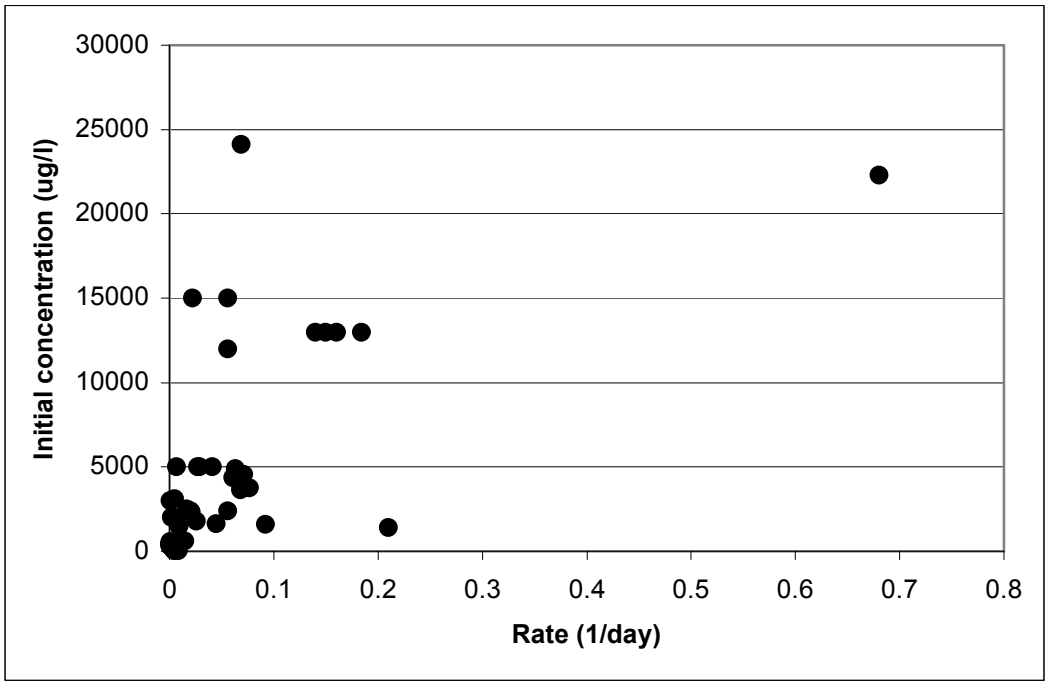


Figure 4.7: Rate of anaerobic *m*-xylene biodegradation as a function of initial contaminant concentration derived from the data compiled by Arenson & Howard (1997). Experimental data reported by Arenson & Howard that included both contaminant concentration and a biodegradation rate were selected for this graph. For those datasets reporting a range of values, only the lowest were taken; for rate data designated as less or more than a specified rate, the value for plotting was taken to be equivalent to the stated rate. No distinction was made between experiment type or temperature.

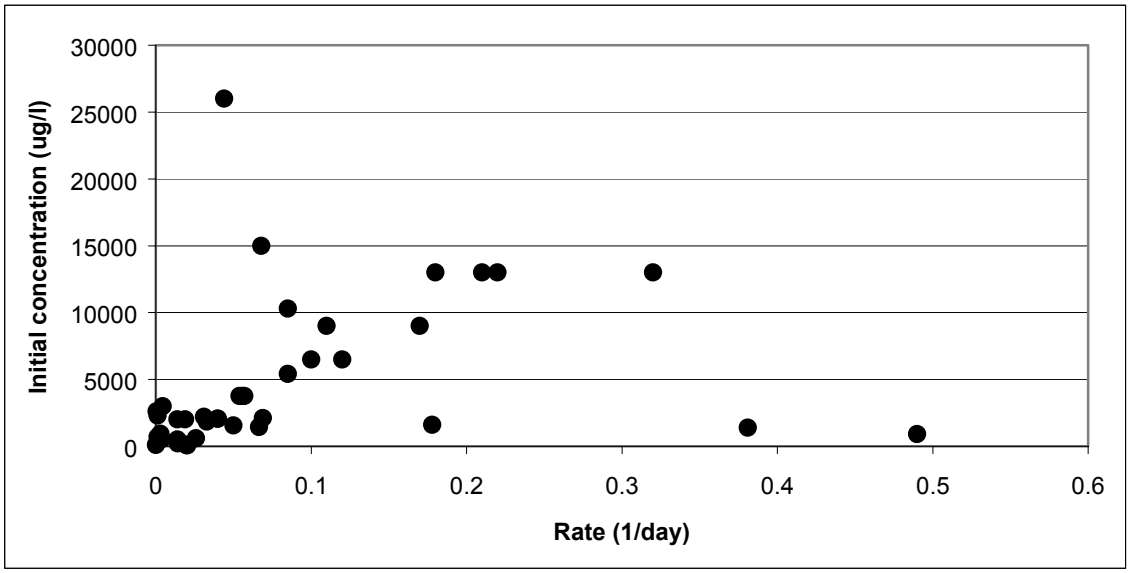


Figure 4.8: Rate of anaerobic *p*-xylene biodegradation as a function of initial contaminant concentration derived from the data compiled by Arenson & Howard (1997). Experimental data reported by Arenson & Howard that included both contaminant concentration and a biodegradation rate were selected for this graph. For those datasets reporting a range of values, only the lowest were taken; for rate data designated as less or more than a specified rate, the value for plotting was taken to be equivalent to the stated rate. No distinction was made between experiment type or temperature.

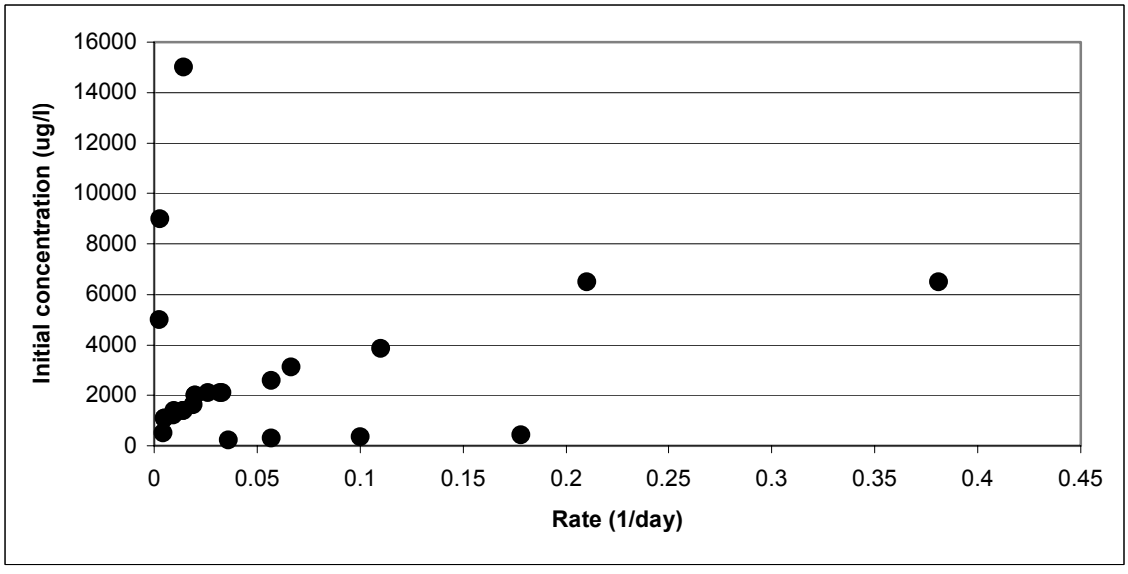


Figure 4.9: Rate of anaerobic naphthalene biodegradation as a function of initial contaminant concentration derived from the data compiled by Arenson & Howard (1997). Experimental data reported by Arenson & Howard that included both contaminant concentration and a biodegradation rate were selected for this graph. For those datasets reporting a range of values, only the lowest were taken; for rate data designated as less or more than a specified rate, the value for plotting was taken to be equivalent to the stated rate. No distinction was made between experiment type or temperature.

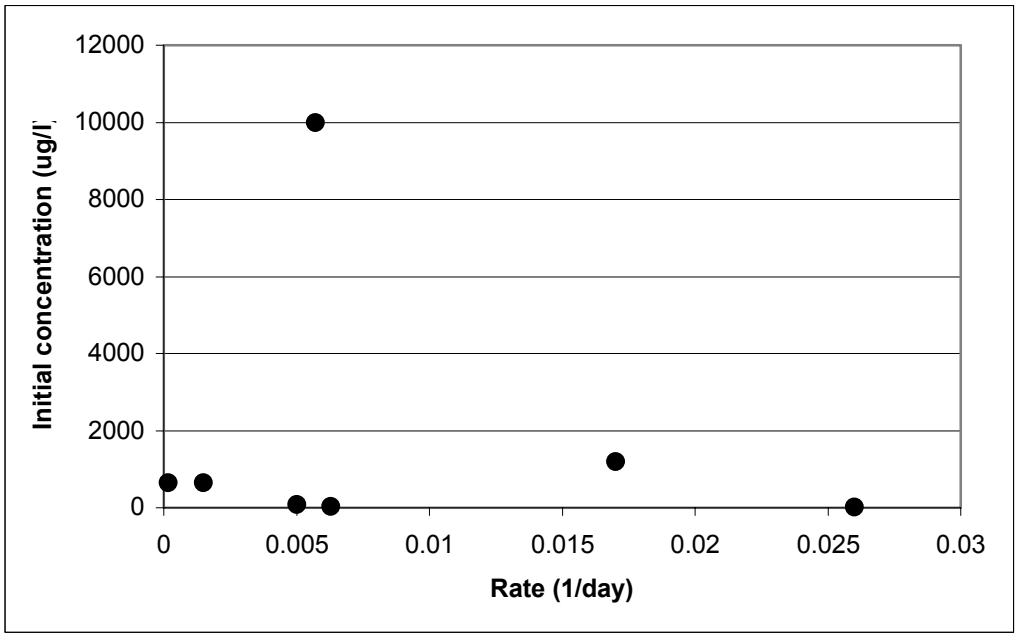


Figure 4.10: Rate of anaerobic phenol biodegradation as a function of initial contaminant concentration derived from the data compiled by Arenson & Howard (1997). Experimental data reported by Arenson & Howard that included both contaminant concentration and a biodegradation rate were selected for this graph. For those datasets reporting a range of values, only the lowest were taken; for rate data designated as less or more than a specified rate, the value for plotting was taken to be equivalent to the stated rate. No distinction was made between experiment type or temperature.

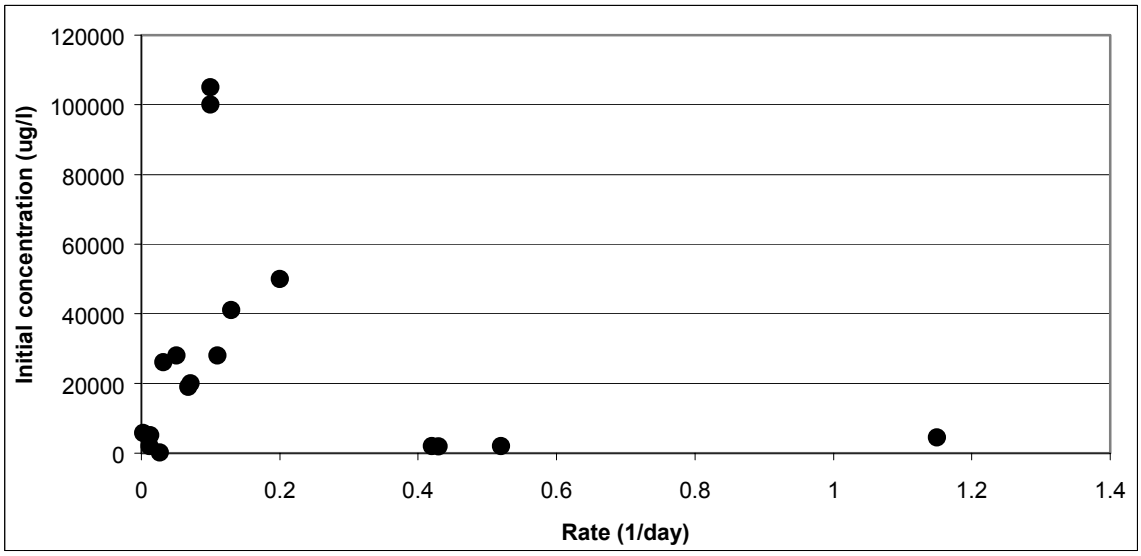


Figure 4.11: Mecoprop stereochemistry and biodegradation

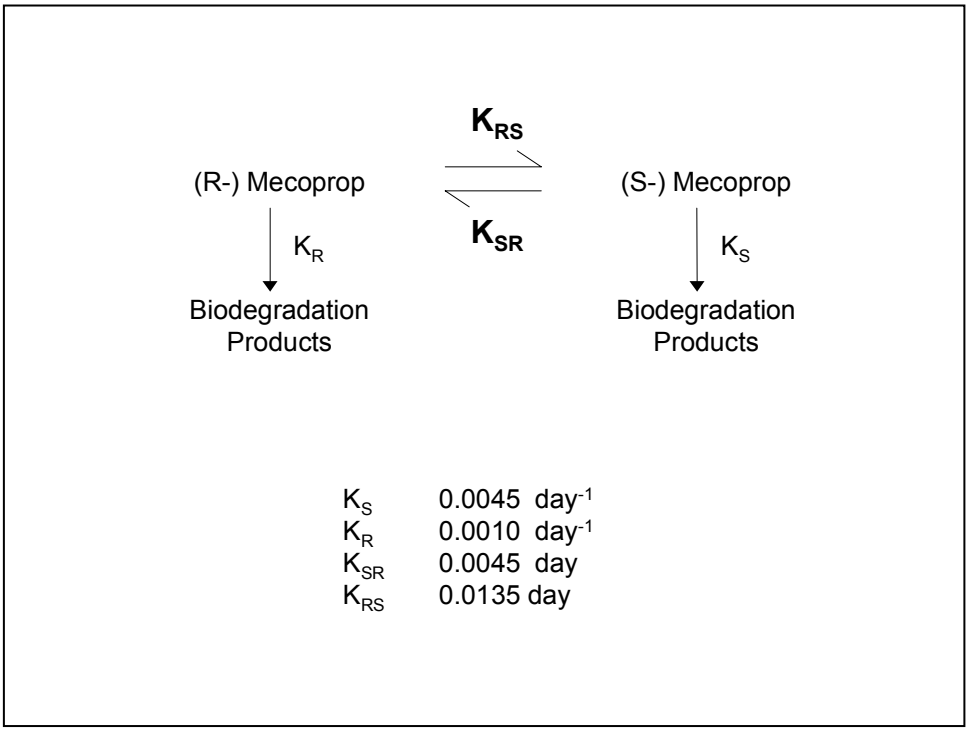


Figure 4.12: Biodegradation pathways for chlorinated ethenes

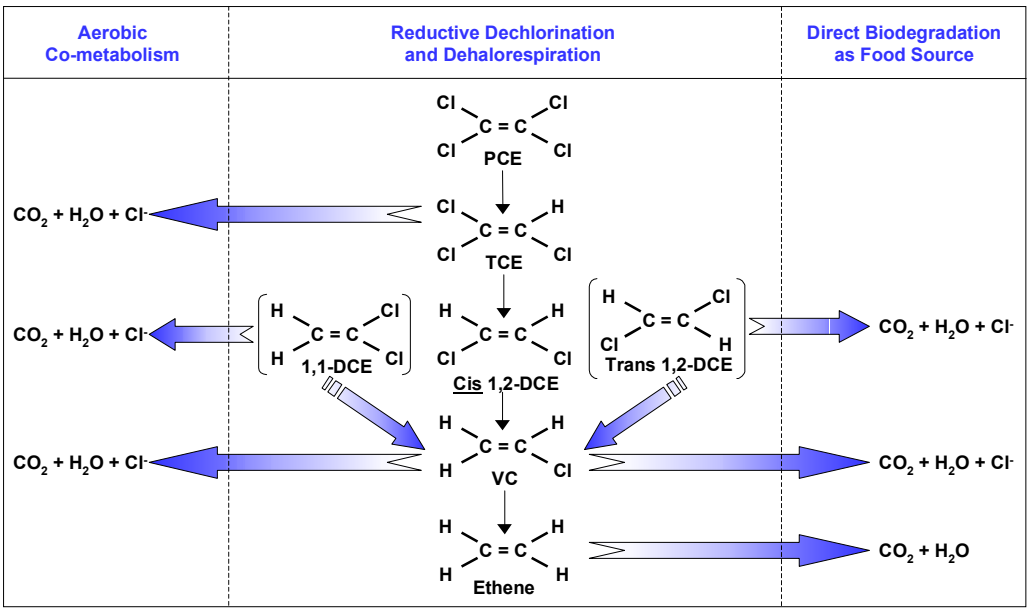


Figure 4.13: Summary of anaerobic biodegradation rates of chlorinated ethenes and ethanes in laboratory and field studies. Shaded bars = lab; open bars = field. Data from Suarez & Rifai (1999).

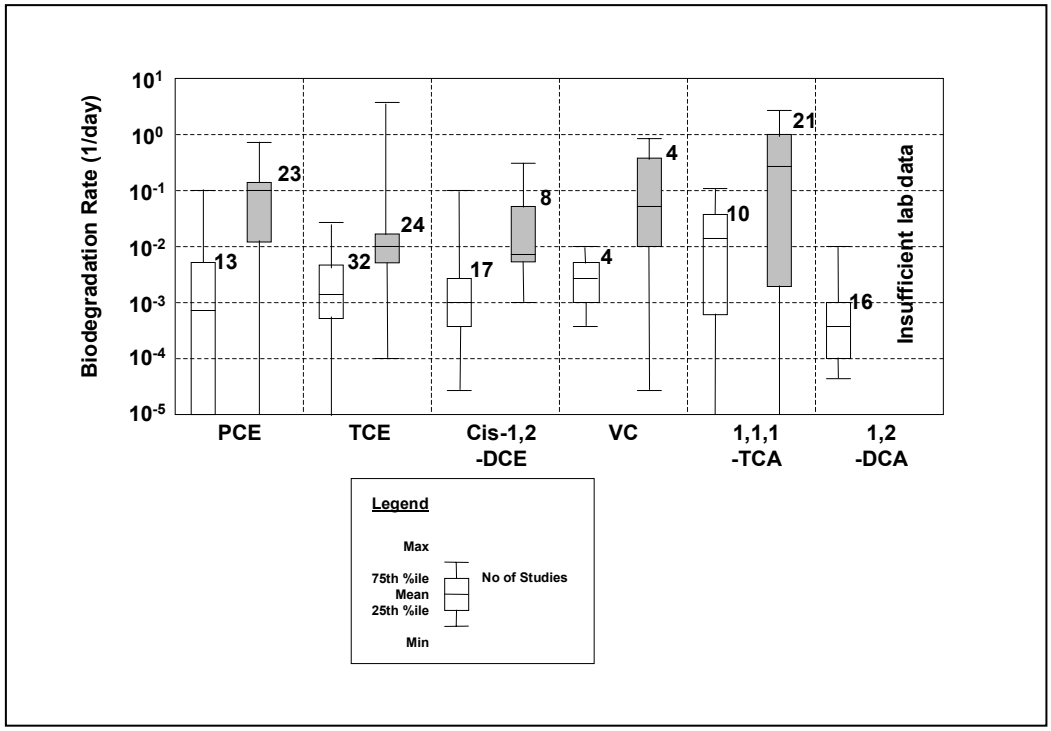


Figure 4.14: Rate of anaerobic PCE biodegradation as a function of initial contaminant concentration derived from the data compiled by Arenson & Howard (1997). Experimental data reported by Arenson & Howard that included both contaminant concentration and a biodegradation rate were selected for this graph. For those datasets reporting a range of values, only the lowest were taken; for rate data designated as less or more than a specified rate, the value for plotting was taken to be equivalent to the stated rate. No distinction was made between experiment type or temperature.

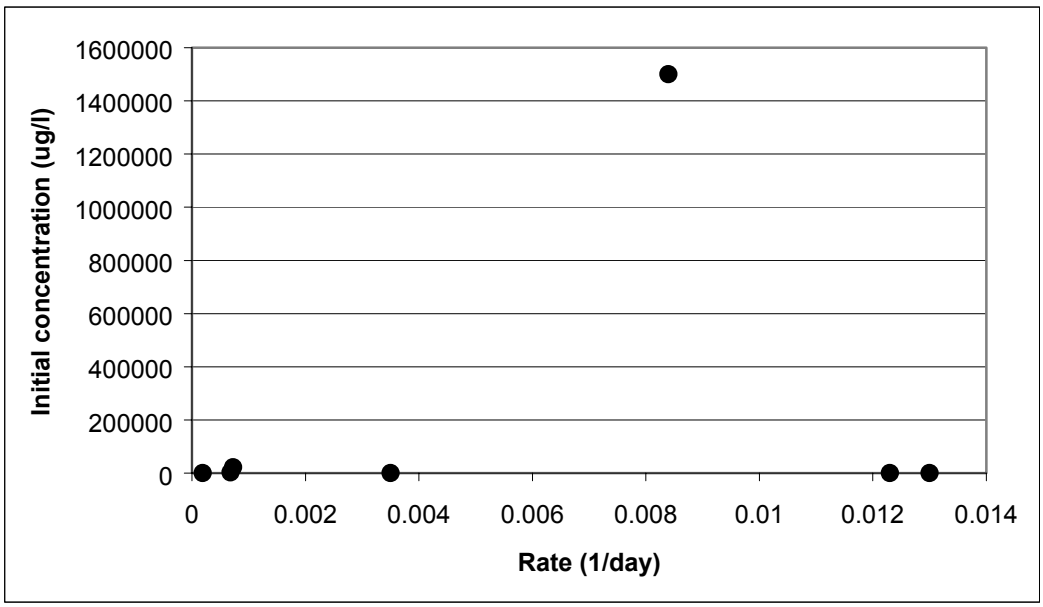


Figure 4.15: Rate of anaerobic TCE biodegradation as a function of initial contaminant concentration derived from the data compiled by Arenson & Howard (1997). Experimental data reported by Arenson & Howard that included both contaminant concentration and a biodegradation rate were selected for this graph. For those datasets reporting a range of values, only the lowest were taken; for rate data designated as less or more than a specified rate, the value for plotting was taken to be equivalent to the stated rate. No distinction was made between experiment type or temperature.

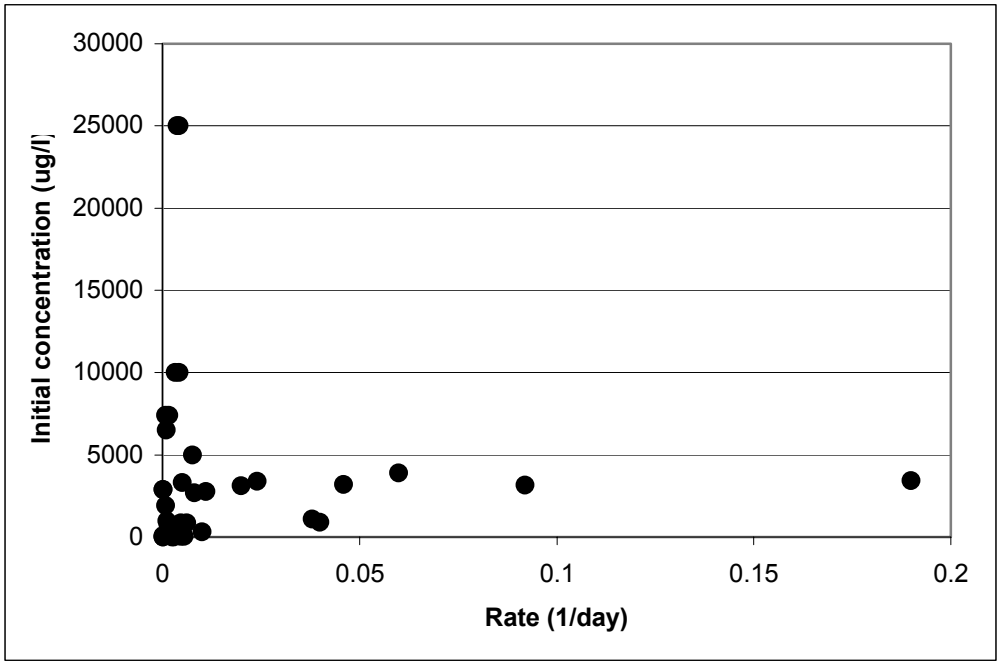


Figure 4.16: Rate of anaerobic vinyl chloride biodegradation as a function of initial contaminant concentration derived from the data compiled by Arenson & Howard (1997). Experimental data reported by Arenson & Howard that included both contaminant concentration and a biodegradation rate were selected for this graph. For those datasets reporting a range of values, only the lowest were taken; for rate data designated as less or more than a specified rate, the value for plotting was taken to be equivalent to the stated rate. No distinction was made between experiment type or temperature.

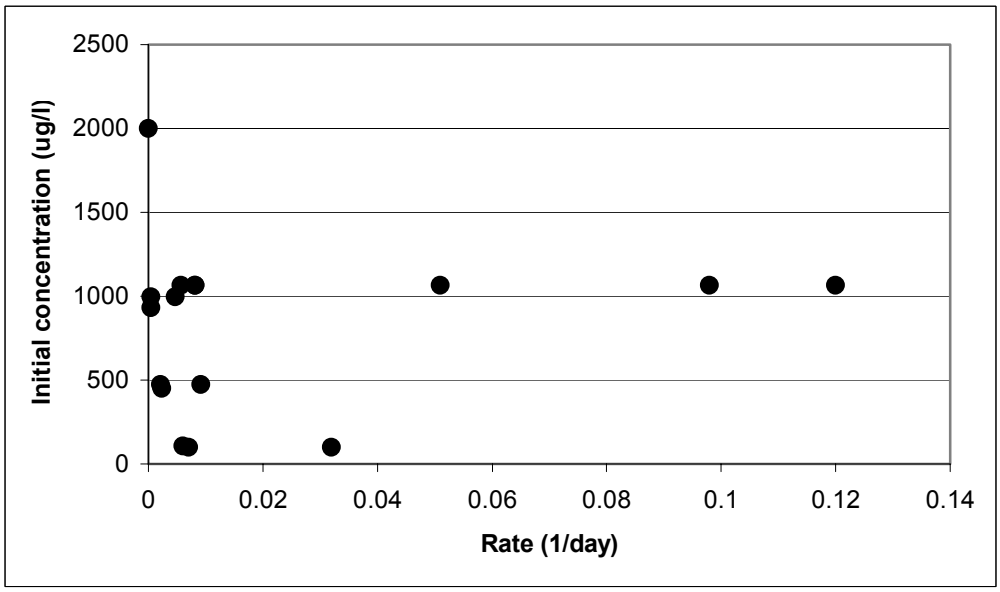


Figure 4.17: Abiotic chemical degradation of 1,1,1-trichloroethane

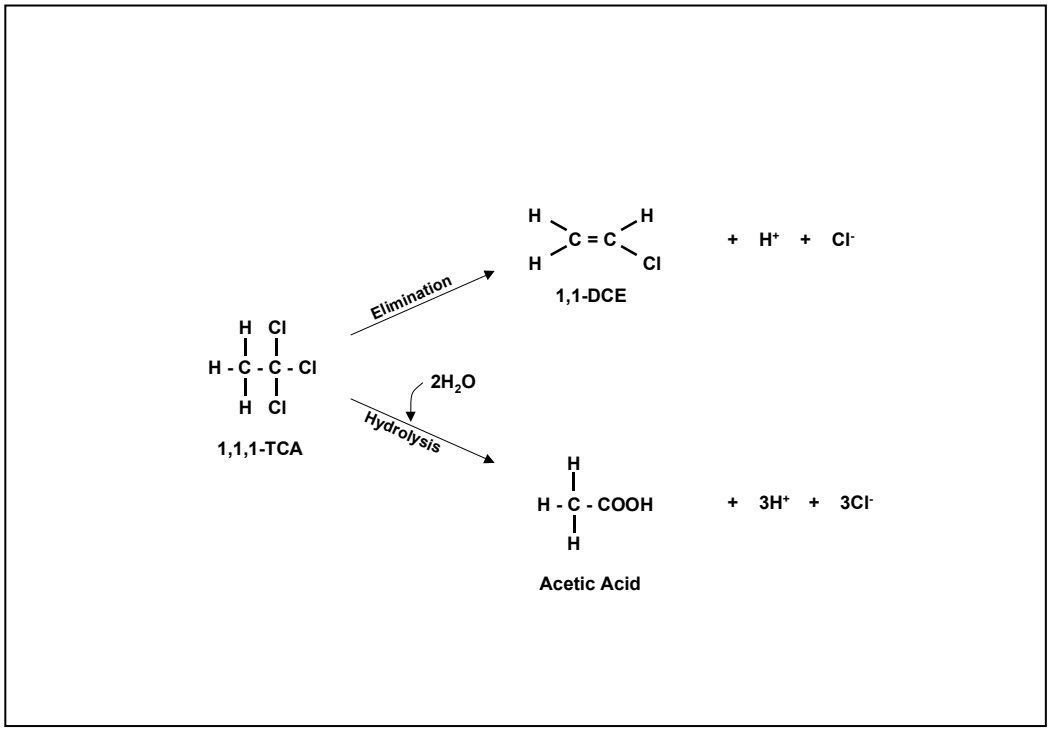
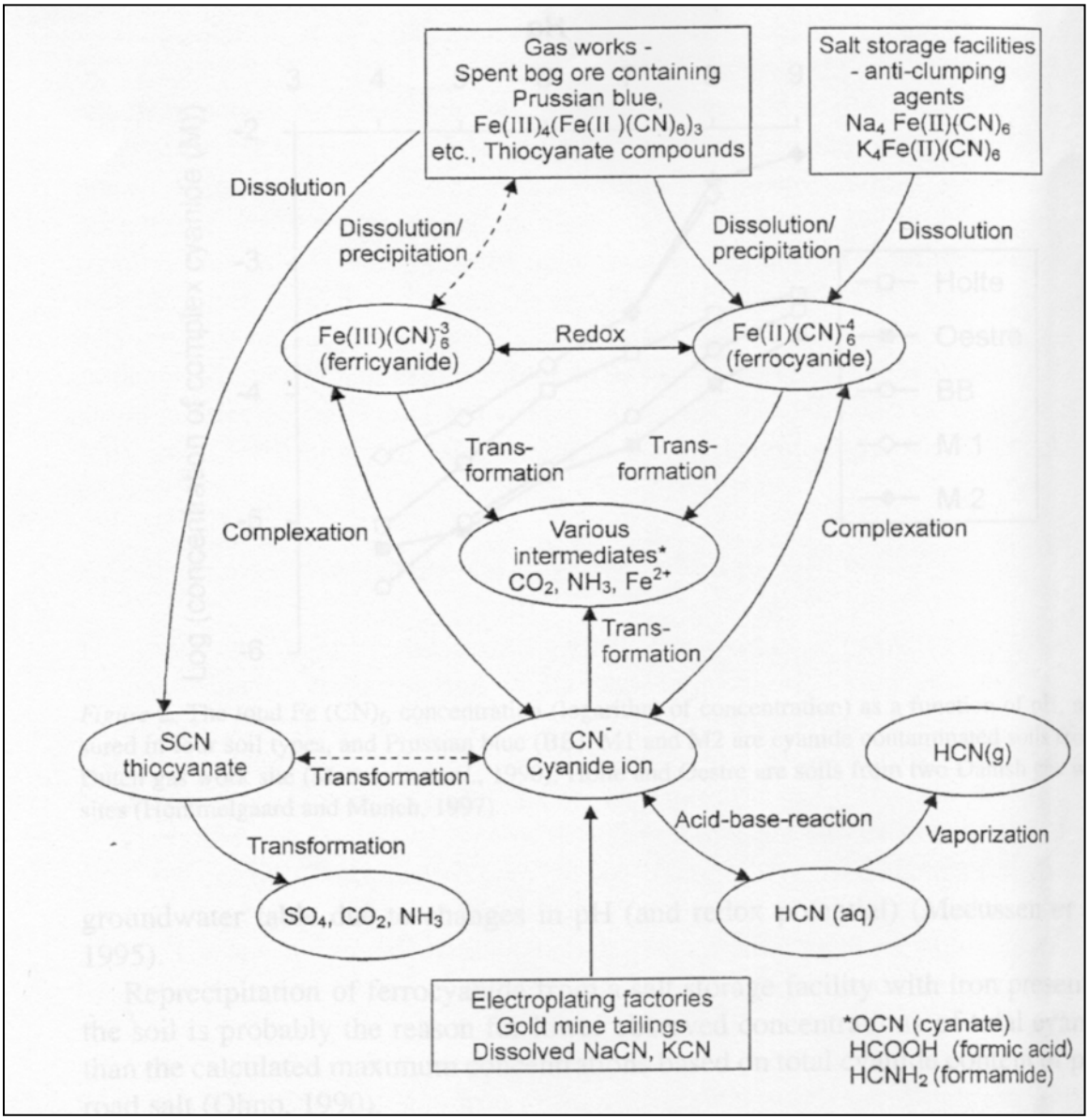


Figure 4.18: Subsurface reactions of major inorganic cyanide species encountered in soil and groundwater (from Kjeldsen, 1999)



APPENDIX 2 : SORPTION PROCESSES

Sorption experiments

Batch testing is a quick and relatively inexpensive method of producing sorption estimates. Batch testing involves placing uncontaminated aquifer materials into a number of reaction vials. Solutions of varying concentrations are added, the vials are sealed and shaken until equilibrium is reached. Each vial represents a data point on a plot of sorbed mass versus contaminant concentration. The slope of this graph (known as the isotherm due to the experiment being conducted at constant temperature) represents the partition (or distribution) coefficient at the concentration of interest. In the case of linear sorption, the slope of the graph is a straight line and K_d is a constant.

Column testing involves placing uncontaminated aquifer material in a laboratory column and passing through contaminant solutions which can be made up in the laboratory or taken from groundwater at the study site. Flow rate and time are controlled and samples are collected from the effluent of the column. The results of column tests can be used in a variety of ways to determine sorption parameters (e.g. calculating average plume velocity and average water velocity, curve fitting models).

Sorption Models

Langmuir, non-linear sorption behaviour describes a case where the sorbed concentration increases linearly with dissolved concentration at low contaminant concentrations and then approaches a constant value at higher contaminant concentrations due to the presence of a limited number of sorption sites in the solid matrix. The Langmuir equation is described mathematically as:

$C_a = KC_lb/(1+KC_l)$, where:

C_a = sorbed contaminant concentration (mass of contaminant/mass soil);
K = equilibrium reaction for the sorption reaction (μg/g);
C_l = dissolved contaminant concentration (μg/ml);
b = number of sorption sites (maximum amount of sorbed contaminant).

Freundlich, non-linear sorption describes a system in which the number of sorption sites is large relative to the number of contaminant molecules but where sorption decreases with increasing contaminant concentration. This model is more suitable for dilute solutions. Weber *et al.* (1992) noted that the concentration-dependent Freundlich isotherm model is suited to describing physical adsorption to heterogeneous sites.

The Freundlich equation is described mathematically as:

$C_a = K_dC_l^{1/n}$, where:

K_d = partition coefficient;
C_a = sorbed contaminant concentration (mass contaminant/mass soil, μg/g);
C_l = dissolved contaminant concentration (mass contaminant/volume solution, μg/ml);
n = chemical specific constant (or Freundlich exponent).

Values of 1/n, which is determined experimentally and can be thought of as representing the degree of non-linearity, typically range from 0.7 to 1.1 but may be as low as 0.3 and as high as 1.7 (Lyman et al, 1992).

This is a special case of the Freundlich isotherm (see Figure 3.1) in which there is a linear relationship between the concentration sorbed and the concentration in solution. The linear model is reported to be valid for a dissolved species that is present at a concentration of less than half of its solubility limit (Lyman *et al.*, 1992).

The linear sorption isotherm is described mathematically as:

$C_a = K_d C_l$ where:

K_d = partition coefficient (slope of the isotherm, ml/g);
C_a = sorbed contaminant concentration (mass contaminant/mass soil, μg/g);
C_l = dissolved contaminant concentration (mass contaminant/volume solution, μg/ml);

A retardation factor, r_f, has been defined as:

$1 + ((B_d/\theta).K_d) = r_f = v_x/v_c$, where,

B_d = bulk density
θ = porosity
K_d = partition coefficient
v_c = average linear groundwater velocity
v_x = average contaminant velocity

Retardation factors, which are a clear way of expressing the magnitude of sorption, are often quoted in sorption-related literature.

Fraction of Organic Carbon (f_{oc})

In most cases, the aquifer fraction of organic carbon (f_{oc}) controls sorption of organic contaminants (Schwarzenbach & Westall, 1981). However, there is a critical level of organic carbon below which sorption to mineral surfaces becomes the dominant sorption mechanism (McCarthy *et al.*, 1981). This critical value of f_{oc} increases with **increasing** surface area of the mineralogical component (i.e., clay content) and **decreasing** K_{ow} (hydrophobicity) of the contaminant. K_{ow}, the octanol-water partition coefficient, is a measure of the hydrophobicity of a compound and is expressed as the ratio of the concentration of a contaminant in *n*-octanol to water at equilibrium under defined test conditions.

Partition coefficient for organic carbon (K_{oc})

A further sorption parameter for a contaminant K_{oc}, (the partition coefficient for organic carbon) is defined as K_d normalised to the aquifer matrix f_{oc}. This has been found to eliminate much of the variation in K_d observed as a result of the variation in f_{oc} content of different formations. If sorption is dominated by the aquifer organic carbon, and the effect of composition of f_{oc} on sorption is ignored and if sorption is assumed to be linear, then:

$$K_d = K_{oc}.f_{oc} \text{ (if non-linear, } K_{oc} \text{ applies to a contaminant concentration of interest)}$$

In systems with high clay content and low organic carbon content and for contaminants with low K_{oc} and hydrophobicity (e.g., benzene), the importance of sorption may be underestimated by this model and the above equation will be a less accurate description of the sorption process.

Composition of F_{oc}

It should also be noted that the assumption that the effect of f_{oc} composition can be accounted for by use of K_{oc} may be too simplistic. Steventon-Barnes (2000) reported that the oxygen content of the organic matter may be influential to the actual partition coefficient, K_d. Since the nature of the organic matter in a geologic strata is normally controlled by the depositional environment and subsequent diagenetic modifications, the magnitude of sorption processes may vary significantly between geologic formations with similar f_{oc} magnitudes but different geologic histories (eg Binger et al 1999 and references there-in).

APPENDIX 3

Kinetic expressions used to estimate destructive attenuation rates

Introduction to the kinetics of chemical reactions

The rate of a chemical reaction is expressed as the variation in the concentration of the original chemical(s) with time. The units of rate normally used by chemists is mol l^{-1} s^{-1} (moles per litre per second).

The rate of reaction for the hypothetical reaction A $\rightarrow$ B + C is given by:

$$-\frac{d[A]}{dt} \qquad (1)$$

Where: $[A]$ = concentrations of reactant A (mol l^{-1})
t = time (seconds).

Reaction order (zero-, first and second-order reactions)

The Law of Mass Action states that the rate of a chemical change varies directly as the active concentration of the reactants.

Taking the simple example reaction A $\rightarrow$ B + C, we shall assume that the rate is directly proportional solely to the concentration of A, i.e. "first order" with respect to A. Then, the rate expression for the reaction can be expressed as:

$$-\frac{d[A]}{dt} = k[A] \qquad (2)$$

Where: k = rate constant.

It should be noted that the use of the Greek letter λ (lambda) is becoming commonplace as the designation for the first order rate constant, particularly in the biochemical literature. However, for the purposes of this report, we shall stick with use of the more widely recognised abbreviation *k*.

Since the concentration of A will decrease as the reaction proceeds, so the observed rate of reaction must also decrease with time. However, the rate constant remains unchanged and provides a convenient measure of the reaction velocity. For a first order reaction the unit of the rate constant is normally s^{-1} (1/seconds) but for convenience, environmentally significant rates can often be expressed in other time units.

To determine the rate constant *k* from experimental rate data it is necessary to know the number of concentration terms in the rate expression; the number of these is known as the reaction order. In the above simple example, the rate of reaction is dependent solely on the concentration of contaminant A, hence this is a first-order reaction.

Zero-order reactions are also important in aquifers and are those reactions where the rate of reaction for the contaminant is independent of its concentration. This can arise where the

reaction rate is dependent on the concentration of another factor such as an enzyme or chemical catalyst. For the catalysed reaction X → Y + Z, the zero-order rate expression would be:

$$-\frac{d[X]}{dt} = k[catalyst] \tag{3}$$

Where: [*catalyst*] = concentration of the catalyst.

Rarely in MNA cases, a reaction may be second-order, i.e. the rate is proportional to the concentration of two components. For example, if the reaction W + X → Y + Z were dependent on the concentration of both reactants then the second-order rate expression for X would be:

$$-\frac{d[X]}{dt} = k[W][X] \tag{4}$$

Where: [*W*] and [*X*] = concentrations of W and X, respectively.

Monod kinetics

Monod kinetics (Monod, 1949) describe the growth of micro-organisms on a substrate that is growth-limiting (i.e., it is assumed that all other requirements are present in excess) and assumes that biomass increase takes place as a result of the biodegradation of that substrate. The kinetics can be represented mathematically by:

$$\mu = \mu_{\max} \frac{S}{S + K_S} - k_d \tag{5}$$

Where:

μ	=	growth rate (hour^{-1})
μ_{max}	=	maximum growth rate (hour^{-1})
S	=	substrate concentrations (mg l^{-1})
K_s	=	half-saturation constant (mg l^{-1}; that substrate concentration that allows the microorganisms to grow at half of the maximum rate)
k_d	=	microbial decay rate ("death rate"; hour^{-1})

The change in substrate concentration is given by:

$$\frac{dS}{dT} = -\frac{\mu_{\max}}{Y} B\left(\frac{S}{K_s + S}\right) \tag{6}$$

Where:

Y	=	biomass yield (mg biomass mg substrate utilised^{-1})
B	=	biomass concentration (mg l^{-1})

It is apparent from the above equations that reliable estimates of K_s, μ_{max}, Y and k_d are essential for the reliable derivation of biodegradation rates using Monod kinetics. Since these variables are highly specific to the case under consideration, the practical use of Monod kinetics is confined to laboratory studies where these variables can be determined.

At low substrate concentrations (when $[S] << K_s$) biological reactions approximate to first order reactions, provided it is assumed that no significant change in biomass takes place. This assumption is the one normally made for the field (and many laboratory) determinations of biodegradation rate in groundwater and is reasonable at the dissolved phase concentrations of many contaminants.

Conversely, at high contaminant concentrations (when $[S] >> K_s$) then it is commonly assumed that the biologically catalysed reactions can be considered zero-order with respect to the contaminant. For example, Haston & McCarty (1999) noted that zero-order kinetics were more appropriate to describe the reductive dechlorination of chloroethenes than first-order at concentrations "above a few micromolar". It should be noted that zero-order kinetics again assume that no significant change in biomass takes place.

Contaminant half-life

Contaminant half-life has the advantage of being much easier to understand intuitively that rate constant and gives the end-user an approximate feel for the longevity of a contaminant in groundwater. Half-life ($t_{½}$) is the time required for the original chemical concentration to be reduced to exactly one-half of its initial concentration.

To derive half-life, it is taken that the reaction under consideration is first-order. Then, integrating equation (2) gives:

$$k = \frac{1}{t} \log_e \frac{[A]_0}{[A]_t} \tag{7}$$

So, at $t = t_{½}$:

$$[A]_t = \frac{[A]_0}{2} \tag{8}$$

and equation (7) may be rearranged to give:

$$t_{½} = -\frac{\log_e 2}{k} \tag{9}$$

or:

$$t_{½} = -\frac{0.693}{k} \tag{10}$$

Equation (10) provides a convenient expression to convert rate constants to reaction half-life. For most reactions in aquifers the reaction half-lives are usually stated in days, months or years.

Effect of temperature on degradation rate

The rates of most chemical reactions increase with a rise in the temperature. Examination of the rate expression:

$$\text{Reaction rate} = k \times (\text{reactant concentration})^{\text{order of reaction}}$$

shows that the k (rate constant) is a temperature-dependent variable and is itself independent of reactant concentration.

In 1889, Arrhenius discovered that the experimentally observed variation of the rate constant (k) with absolute temperature T (expressed in Kelvin) can be expressed as:

$$\log_e k \propto 1/T \qquad (11)$$

or:

$$\log_e k = B - C/T \qquad (12)$$

where B and C are constants for the particular reaction.

An alternative form of this relationship has become known as the Arrhenius equation. This is:

$$\log_e k = \log_e A - E/RT \qquad (13)$$

or, rearranging:

$$k = Ae^{-E/RT} \qquad (14)$$

Where:
- A = "frequency factor";
- E = activation energy for the reaction;
- R = gas constant (0.08206 m^3 atm^{-1} kg^{-1} mol^{-1} K^{-1}).

If A and E are known for a reaction, then the rate constant k can be calculated for a given temperature. Similarly, a plot of $\log_e k$ against 1/T will give a straight line and allows ready extrapolation of rates between temperatures.

Effects of temperature on biodegradation is more complex because the degradation is catalysed by enzymes, which differ in their optimum and maximum operating temperatures. For the purposes of groundwater, enzyme inactivation by high temperature can be disregarded and over a realistic range of groundwater temperatures reported in biodegradation studies world-wide (5 to 30ºC), we can apply the following equation (Metcalf & Eddy Inc., 1991):

$$k_{T1} = k_{T2} \cdot \theta^{(T1-T2)} \qquad (15)$$

Where:
- k_{T1} = Rate constant at temperature 1
- k_{T2} = Rate constant at temperature 2
- T1 = Temperature 1
- T2 = Temperature 2
- θ = Empirical temperature correction coefficient

The value of the temperature correction coefficient θ is specific to the microbial population and may vary between 1.03 and 1.135 (Metcalf & Eddy Inc., 1991).

For simplicity of calculation when specific values of θ are not available, it can be useful to apply the concept of Q_{10} to extrapolate biodegradation rates between different temperatures. Q_{10} is the factor by which a biodegradation rate changes as a result of a 10°C change of temperature. For normal ambient temperatures a Q_{10} value of 2.0 is often applied, i.e.:

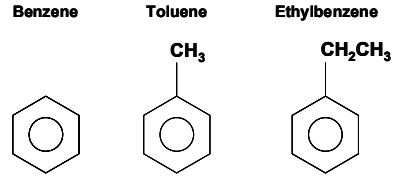
Rate at 10°C x 2.0 = Rate at 20°C
Rate at 20°C x 2.0 = Rate at 30°C

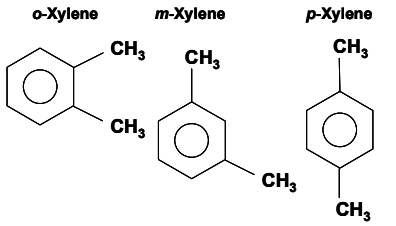
When measured for specific cases, Q_{10} will differ in exactly the same way as θ, but can be used as a pragmatic "rule of thumb" to account simply for temperature changes.

APPENDIX 4

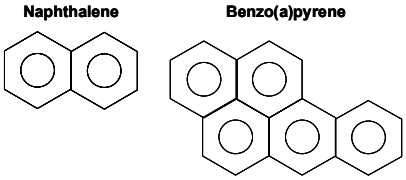
Molecular structures of organic compounds evaluated in this report.

BTEX components

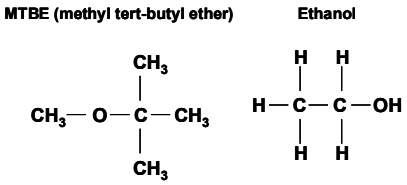




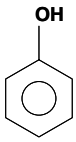
Polycyclic aromatic hydrocarbons



Fuel additives

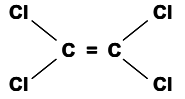


Phenol

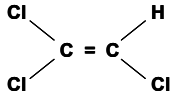


Chlorinated solvents

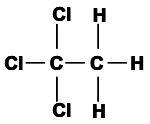
Tetrachloroethene (PCE)



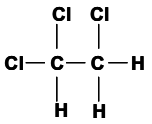
Trichloroethene (TCE)



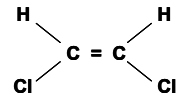
1,1,1-trichloroethane



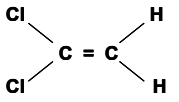
1,1,2-trichloroethane



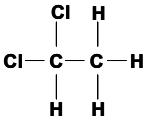
cis-1,2-dichloroethene (*cis*-1,2-DCE)



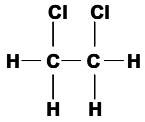
trans-1,2-dichloroethene (*trans*-1,2-DCE)



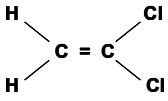
1,1-dichloroethane



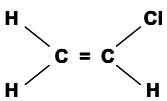
1,2-dichloroethane



1,1-dichloroethene 1,1-DCE

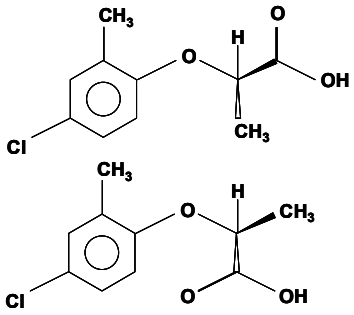


Vinyl Chloride

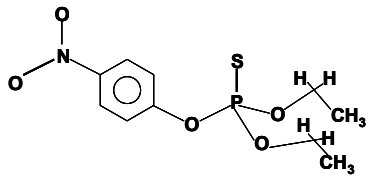


Pesticides

Mecoprop [2-(2-Methyl-4-chlorophenoxy) propionic acid]



Parathion [O,O-diethyl-O-*p*-nitrophenylthiophosphate]



APPENDIX 5 Summary of literature database search strategy

1. Search strategy

MNA is a relatively young science and therefore much potentially useful data may either be as yet unpublished or is only available from the "grey literature" (conference proceedings, etc.). Therefore, standard information searches using on-line literature databases (e.g., Chemical Abstracts) may omit a significant proportion of information important in a project such as this. Therefore, the literature search strategy applied in this project was to combine on-line database searches with access to the "grey literature" and unpublished results obtained from a variety of organisations.

The details of the literature searching process are given in below. A total of approximately 300 individual published papers, 20 conference proceedings books and 10 other sources of information identified by the literature search were taken forward for screening.

The screening process involved an assessment of whether the identified references contained data on the effect of concentration on natural processes for the specified contaminants or whether a reliable estimate of this could be obtained from the data presented. Duplicate sources of information were also eliminated at this stage; this applied particularly to data from conference proceedings that had subsequently appeared in peer reviewed publications. From this screening, 200 references were taken for evaluation.

Literature review papers that contained compilations of attenuation rate data were not evaluated alongside references containing specific data, since in most cases the reviews did not provide specific information that would influence interpretation of individual case data. However, appropriate reviews were used to validate the rate data compiled and extend the range of the dataset.

2. Evaluation and interpretation process

Potentially relevant literature identified from the screening programme was reviewed to extract and interpret the relevant data. Unpublished results were processed separately.

The initial stage of evaluation was the generation for each reference of a summary sheet to capture relevant information in a consistent format. Where the reference contained a direct estimate of natural attenuation process rates and/or contaminant concentrations then these were taken directly for further consideration. Where the reference lacked this information directly, then an evaluation was made whether it could be derived by interpolation (for example from graphical plots) or calculation (e.g. from data tables) and then the appropriate derived data was recorded.

For convenience in this report and ease of cross-reference, the key data from the summary sheets has been transposed onto a single summary table (Appendix 5) in which all rate data have been translated into half-life estimates for reasons of consistency. Where rate data were converted into half-lives then it was assumed that these data were first order and converted accordingly (Appendix 2). This may not be strictly accurate for those papers that report or imply zero-order or Michaelis-Menten kinetics but this is unlikely to be a major error relative to the other site variables and experimental inconsistencies between reports.

It is important to note that many papers reporting biodegradation data attempt to factor out abiotic attenuation mechanisms, both destructive and non-destructive, when deriving rates from the field. However, this is not always the case and in some cases reported data are inadequate to enable a distinction to be made between processes. These papers were disqualified from further evaluation; MNA screening based on such data used alone may significantly overestimate attenuation rate unless appropriate correction is made for differences in contaminant transport, dispersion and dilution between aquifers.

A significant proportion of papers on biodegradation give rate data obtained under conditions that will give a combination of aerobic and anaerobic biodegradation. Therefore, reported rates may actually reflect a combination of aerobic and anaerobic biodegradation. Since anaerobic conditions are likely to predominate in such systems, these data were classified as anaerobic biodegradation unless the source reference gave a clear indication that aerobic conditions were the most important.

Once data had been compiled onto the sheet in Appendix 5, it was reviewed to determine whether the datasets included sufficient information on concentration, rate and other variables to merit further evaluation. Those that were considered appropriate were transferred onto data compilation sheets for each individual compound considered in this report. These are presented in Appendix 6 and include conversion to a standard UK aquifer temperature of 10°C based on the Arrhenius relationship for chemical degradation processes and an assumed Q_{10} value of 2.0 (Appendix 2), which will be relatively conservative in extrapolating rates determined at higher ambient temperatures to the standard groundwater temperature (10ºC) applied. It was remarkable how many papers did not clearly report temperature; rather than exclude this potential dataset from inclusion, we assumed a temperature of 20°C (common in many laboratory studies) and corrected accordingly; this would be conservative in the majority of cases.

Where a reference contained information of more general applicability but lacks specific data on rate versus contaminant concentration then it may be discussed specifically in Section 5.1 of this report even though it is not present in the table.

3. Analysis of unpublished site information

The derivation of information from unpublished data relating to UK sites is given in Appendix 7. The information is included in the data compilation in Appendix 6 and/or the discussion sections of this report, as appropriate.

4. Validation

Preliminary screening of rate data gathered from the reviewed references was compared with a number of previously published review papers to confirm that the ranges and spread of data obtained were in-line with the broad range of reported values. The previously published review papers used for this purpose were: Suarez & Rifai (1999); Kolhatkar *et al*. (2000); Wilson *et al*. (1997); Lee *et al*. (1998); Wiedemeier *et al.* (1998); Industrial members of the RTDF Bioremediation Consortium (1997); Christensen *et al*. (1994); Aronson & Howard (1997); Montgomery (1996); Howard *et al*. (1991); Verschueren (1996).

The individual data derived for this report from the unpublished cases summarised in Appendix 7 were cross-checked for accuracy by those who provided the original information.

The overall dataset and the conclusions drawn were validated by independent peer review.

5. Database Search Strategy

The following databases were searched *via* the STN host:

- Chemical Abstracts Registry file
- Chemical Abstracts (bibliographic file HCAPlus)
- BIOSIS (Biological Abstracts)
- GeoRef
- Pollution Abstracts

Procedure

Chemical Abstracts Registry file searched to find Registry numbers for all the compounds, including isomers.

Chemical Abstracts (bibliographic file) searched using these Registry numbers for the compounds, linking these with the agreed groundwater and degradation keywords. The occurrence of all the keywords was limited to titles only. Three other three files were then searched simultaneously and further novel hits were retrieved (duplicate removal command used between the files). Keywords (chemical names) were used for the compounds in the non-Chemical Abstracts files as Registry numbers were not available and again restricted the occurrence of the groundwater and degradation keywords to titles only. See attached *Search Logic 1*, below.

Titles and accession numbers printed for references from the above search. These were screened manually and then bibliographic information and abstracts were obtained and printed for the titles of interest (searched on accession numbers).

There was little information obtained using the above method for four of the compounds: parathion, cyanide (inorganic), benzo(a)pyrene and ethanol (linked to gasoline, automotive etc). These were therefore searched for again on the databases (excluding Pollution Abstracts as this had produced few additional useful references from the first search). The same keyword combinations were used but the groundwater and degradation terms were not restricted to occurring in the titles only. (They could therefore appear in the abstracts or indexing terms as well as the titles). See attached *Search Logic 2*, below.

Titles and accession numbers for references from above search were printed and manually screened. Titles of interest were used to obtain and print bibliographic information and abstracts (searched on accession numbers).

A final check was made for benzo(a)pyrene and all files were searched (multiple search) for any additional references which may have been missed as a result of the use of alternative spellings. Three such references were found and printed with abstracts. See attached *Search Logic 3*, below.

Search logic 1 for Chemical Abstracts

s 108-95-2 or 71-43-2 or 108-88-3 or 100-41-4 or 1330-20-7 or 91-20-3 or 50-32-8 or 1634-04-4
s 127-18-4 or 79-01-6 or 75-35-4 or 156-59-2 or 156-60-5 or 25323-30-2 or 75-01-4 or 71-55-6
s 75-34-3 or 107-06-2 or 1300-21-6 or 544-92-3 or 143-33-9 or 151-50-8 or 74-90-8
s 64-17-5 and (gasoline or petrol)
s 7085-19-0 or 28473-03-2 or 94596-45-9 or 2786-19-8 or 56-38-2 or 298-00-0
s groundwater/ti or aquifer#/ti
s biodegrad?/ti or degrad?/ti or minerali?/ti or breakdown/ti or attenuat?/ti or hydrolys?/ti
s adsor?/ti or absor?/ti or desor?/ti or sorption/ti or fate/ti
s (l1-l5) and l6 and (l7 or l8)

Search logic for files BIOSIS, GeoRef and Pollution Abstracts (multifile search)

s phenol or benzene or toluene or ethylbenzene or xylene# or naphthalene or benzo[a]pyrene
s btex or mtbe or tetrachloroethene or trichloroethene or dichloroethene or vinyl()chloride
s ethanol and (gasoline or petrol)
s trichloroethane or dichloroethane or cyanide or mecoprop or parathion
s ethyl benzene or benzo(a)pyrene or tetrachloro()ethene or trichloro()ethene
s dichloro()ethene or trichloro()ethane or dichloro()ethane
s groundwater/ti or aquifer#/ti
s biodegrad?/ti or degrad?/ti or minerali?/ti or breakdown/ti or attenuat?/ti or hydrolys?/ti
s adsor?/ti or absor?/ti or desor?/ti or sorption/ti or fate/ti
s (l1-l6) and l7 and (l8 or l9)

Duplicates were then removed using the DUP REM command.

Search Logic 2

s 50-32-8 or benzo(a)pyrene
s 544-92-3 or 143-33-9 or 151-50-8 or 74-90-8 or cyanide
s 64-17-5 or ethanol and (gas? or petrol? or automo? or car#)
s 56-38-2 or parathion
s groundwater or aquifer#
s biodegrad? or degrad? or minerali? or breakdown or attenuat? or hydrolys?
s adsor? or absor? or desor? or sorption or fate
s l1 and l5 and (l7 or l8)
s l2 and l5 and (l7 or l8)
s l3 and l5 and (l7 or l8)
s l4 and l5 and (l7 or l8)

Duplicates were removed using DUP REM command
Search Logic 3

50-32-8 or benzo(a)pyrene
s groundwater or aquifer
s biodegrad? or degrad? or minerali? or breakdown or attenuat? or hydrolys?
S ADSOR? OR ABSOR? OR DESOR? OR SORPTION OR FATE
s l1 and l2 and (l3 or l4)
s benzopyrene or benzpyrene or 3()d()concord
s l6 and l2 and (l3 or l4)
s l7 not l5

APPENDIX 6

Literature review summary table

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
									25	ug/l	6-9	
Davidson et al	1980	x		4 Sites, USA	25	Parathion	x		10000	ug/l	No degradation	14C mineralisation
Jury et al	1987	x		Generic USA	nq	Parathion	x	x	nq		18	
Sims & Abbott	1992	x		USA	20-22	naphthalene, B(a)P	x		900	mg/kg	No degradation	95% incorporated into soil Humics
						Toluene		x	2	mg/l	16-30	
Borden et al	1997	x		SB Site USA	16 (Lab)	B, E, X		x	2	mg/l	No degradation	
						B		x	2	mg/l	28	
						T		x	2	mg/l	15	
		x		RP Site, USA	16 (Lab)	E, X		x	2	mg/l	35	
						B		x	nq		30-141	
Borden et al	1997		x	RP Site, USA	nq	X		x	nq		48	Total xylenes
						B		x	nq		3465	
						T		x	nq		330	
Borden et al.	1997		x	USA	nq	X		x	nq		330-550	Total xylenes
Meehan et al	1999	x		2 sites, Australia	16-24	Cyanide	x		1-100	mg/l	1-2	No degradation above 56 mg/l
						Cyanides	x	x	<0.4	mg/l	28	
Abou - Rizk et al	1995	x		USA	nq	Phenol	x	x	<0.6	mg/l	21	
Ghosh et al	1997	x	x	USA	nq	Cyanides	x	x	6	mg/l	No degradation	No degradation of complexed cyanides
White & Markwiese	1994		x	USA	25	Cyanide	x		<6	mg/l	10	99% in 13days@6mg/l = rate 0.45/day
Williams et al	2001		x	Helpston, Lincolnshire	10-12	Mecoprop	x	x			See body text	See body text
								x	1/1.8	mg/l	843.0	
								x	0.03-0.8	mg/l	149	
						TCE		x	0-0.3	mg/l	843	
								x	1.5- 9.1	mg/l	28	
								x	0.2-1.5	mg/l	169	
						DCE		x	0-0.2	mg/l	1265	
Weaver et al	1997		x	St Joseph, MI	nq	VC		x	0.4-1	mg/l	253	
Wiedemeier et al			x	Plattsburg AFB, NY				x	VC 0.1 -0.4	mg/l	632	
								x	VC = 0.01	mg/l	25295	

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
					nq	TCE, BTEX, DCE, VC		x	TCE h. anaer	1.24	204	BTEX, 0-17 mg/l
								x	TCE anoxic	0	0	TCE 0-25 mg/l
								x	DCE h anaer	0.03	8432	
								x	DCE anoxic	0.07	3614	
								x	VC h anaer	0	0	
								x	VC anoxic	0.47	538	
Wilson et al		x	x	Tibbetts Road, Barrington, NH				x	BTEX h anaer	0.1	2529	
								x	BTEX anoxic	0.39	649	
					10	TCE, B, T	x	x	0.33-0.4mg/l			
									TCE Lab	3.69	69	
									B Lab	2.36	107	
									T Lab	3.63	70	
									TCE Field	0.59	429	
Yager et al		x		Niagara, NY					B Field	0.82	308	
Ellis et al			x	Dover AFB, DE					T Field	1.42	178	
Dupont et al			x	Eielson, Alaska		TCE, DCE		x	26 mg/l TCE		TCE->DCE 66; DCE->VC 140	conc quoted as 0.2mM
Bradley et al		x		Cecil Field, FL	nq	TCE, PCE, DCE, VC	x	x	15mg/l - b/ground		PCE->TCE 949; TCE->DCE1278; DCE->VC 766; VC->ETH 730	converted from T1/2 years
Bradley & Chapelle		x		Cecil Field, FL		TCE		x	<90mg/l		1066	K quoted
Bradley et al		x	x	Plattsburg AFB, NY	nq	VC, DCE	x	x	nq		VC aer<5; DCE aer 28 VC aer + Humus 14; DCE aer + humus v slow	

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
Bradley & Chapelle		x		Cecil Field, FL	Room	DCE, VC	x	x	0.1mg VC; 0.66mg DCE		DCE aer 28; VC aer 5-42 VC Fe red'n 12; VC SR 50	1um VC; 5um DCE
					nq	VC		x	Field 0.008-0.42mg/l		53	Field 8-420ug/l calc T1/2 from rate
					22	DCE, VC	x		0.02-7.8	mg/l		conc covert from umol
									DCE	2		T1/2 calc from umol with conversion in calc
									DCE	4	0.27	
									DCE	8	0.22	
									DCE	15	0.46	
									DCE	28	0.75	
									DCE	40		
									DCE	57		
									DCE	80	1.28	
									VC	2	0.09	
									VC	4	0.13	
									VC	8		
									VC	15		
									VC	28	0.21	
									VC	40	1.08	
Barlaz et al		x	x	Rocky Point, NC					VC	57	0.40	
									VC	80		
					~16	BTEX		x	10mg/l BTEX total lab ~4mg/l spike field test			
									B lab	2.37	29	rate quoted as %/day 10mg/l lab, 4mg/l lab
									B field	0.41	169	
									T lab	4.46	16	
									T field	1.15	60	
									mpX lab	2.04	34	
									mpX field	1.43	48	
									oX lab	5.59	12	
									oX field	<DL		
Wilson et al		x	x	Traverse City, MI					E lab	0.19	365	

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
									E field	<DL		
					nq	BT X	x	x	Sum aromatics 36-40mg/l at core			rate K as /week
									B field	0.05	97	
									B lab	0.5	10	
									T field	1.3	4	
									T lab	0.3	16	
									mpX field			
									mpX lab	0.4	12	
									oX field			
									oX lab	0.5	10	
MacFarlane et a			x	Baltimore, MD					Total field	0.03	162	
Stauffer et al			x	Columbus MI					Total lab			
					nq	N, BTEX		x	nq		B = 729; T=660; E = 877; X's = 855; N = 2166	
					nq	BTEX, N	x		Injection at ~7-70mg/l; 10-50 x dil'n in situ		105	
Wiedemeier et al	1998	x	x	Tibbetts Road, Barrington NH, USA							49	
											110	
					10	BTEX, TCE		x	E BTEX = 7.8mg/l; TCE 1.1mg;l field		308	
Walden & Paersch	1999		x	Duisberg, Germany							305	
											468	
Thierrin et al			x	Perth, Australia	nq	BTEX	?	?	nq		120	
											55	
					21-26	BTEX, naphth	x	x	B<73mg/l; T<92; X's<49; E<8; N<1400mg/l		Aerobic	
											75-160	
											14	

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
Thierrin et al	1993	x	x	Perth, Australia							15	
											15	
					nq	BTEX, naphthalene			0-10mg/l B, T field; 0-~1mg/l lab		No Degn	
											110	
											230	
											223	
											170	
											125	
Bradley & Chapelle	1996	x		Plattsburgh AFB, NY; Cecil Field, FL							160	
Davis & Carpenter	1990	x		Norman, OK								
Kazumi et al	1997	x		Various US	nq	VC	x	x	Field samples <384ug/l; Lab spikes = 17uM		Aerobic ~5; Anaerobic ~13	
Bekins et al		x		Pensacola, FL	20	VC	x		0.1 and 1mg/l		62	
Durant et al	1995	x		Anon, USA	22	B			50um, approx		50-227	
					nq	Phenol (and related)		x	Not given for field except 1 point @ ~25mg/l		46 - 140d *m'genic*	
Aelion	1996	x		Hanahan, SC	22-25	N, B (and other coal gasification components)	x		<20 - 4400ug/l naphth		11-169	
Lerner et al	2000		x	Four Ashes							55-79	
Thornton et al	2000	x			nq	B, T	x?		Lab: concentrations unclear 14c spikedk prob. <<8000ppm on wt bssis		>>100	
						Phenol and related	x	x	B/g - >12000 ppm phenol		20440 to 125195	

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
					18-21	B, T, N, TCA, TCE, PCE			N = 120ug/l; B = 385ug/l; T, TCA, TCE = 550-600ug/l; PCE = 166ug/l		Infinity	
											6.4	
											6 to 20	
											8	
Bright et al	2000	x		UK							46	
											83	
					18-21	BTEX, TCE, PCE, naphth, TeCA, TCA	x	x	N ~120mg/l; TeCA ~166mg/l; BTEX, TCE, TCA, PCE each component ~400-600 mg/l		Negligible	
											26 to 30	
											19 to 22	
											4	
Holman et al		x									12 to 14	
Hanson et al	1999	x		Sediment cores ex-Port Heuneme, CA							19	
Bradley et al		x		Laurens and Charleston, SC	21	Naphthalene	x	x	3.2% diesel (spiked); ~130mg/kg naphth		Aerobic 64-250; Anaerobic = 10000	
Kaseros et a	2000	x			23	MTBE, Ethanol	x		5-20		0.25 to 0.83	
					Room; (~20?)	BTEX, MTBE ex-gasoline	x	x	MTBE 60-140mg/l dissolved phase		80 to 180	
Anderson & Lovley	2000		x	Oklahoma	20	PCE		x	PCE 30um		0.042 to 0.125 approx;	
Ellis et al	2000		x	Dover AFB							0.21 approx	
Carr et al	2000	x			nq	Hydrocarbons - benzene data reported			Up to 100uM		100 to 150	

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
						TCE, DCE			Avg TCE 4.8mg/l; DCE 1.2mg/l		Varied through project due to biomass change. No ral use for this project but half life as low as 1d!	
Leahy & Shreve	2000	x			24	PCE, TCE, DCE, 1,1,1-TCA			Free-phase mixed with aq system		0.16	
											0.11	
Sorenson et al			x	INEEL, USA - TAN area	20	PCE + leachage organics (~110-220ppm BODs)			PCE ~10uM		10 to 20	
Granger et a	1999	x									6 to 10	
Kampbell et al	1996		x	Patrick AFB, CA		PCE, TCE, 1,2-DCE (+ radioisotopes)	x	x	TCE ~1000ug/l @ source 3-4km plume		4745 to 7665	
Alvarez et al	1994			Unnamed, USA	10	Gas condensate (BTEX)	x		<12mg BTEX/l; <187mg/l C12 - C22 HC's		BTEX total 69-1000 days	Phosphorus strongly limited activitry
Klecka et al	1998	x		3 sites in USA	26	BTEX	x	x	0-5000ug/l BTEX. No NAPL		346.5	
					25	T		x	20mg/l		21	
					25	1,2-DCA		x	29mg/l		25	
Johnson et al	2000	x		Hampshire, UK							150	
King et al			x	Borden, Canada							170	
					20 tested	Mecoprop	x		100ug/l		No deg'n in 200d	
					~10	Phenol, X, N	x	x			99	
Broholm & Arvin	2000	x		Mansfield, UK							265 to 1215	
Bouwer et al	1998	x		Unnamed							78 - 95	
					10	Phenol	x	x	5-600mg/l total phenolics		1.35 to 0.89	

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
					22	B, T, N	x	x	<50mg/l		50 to 100	
Furlong et al			x	Bemidji, MN							80 to 160	
											50 to 150	
Chiang et al	1989	x	x	Unnamed, USA	nq	N	x	x	BTEX = 1-190ug/l; N = <1-300ug/l		0.5 to 28	
Chapelle et a	1996	x	x	Hanahan, SC							25 to 258	
					~15 field; ~10 lab	B, T, X	x	x	<10ug/l BTEX field; <20mg/l lab		5 to 20	
Bjerg et al	1996		x	Vejen, Denmark	nq	B, T		x	Lab: T = 90ug/l; B = 600ug/l		23 to 84	
											231	
					10	B, T, oX, N	x		0-200ug/l each		1.39	
											1.73	
Angley et al	1992	x		Lake Alfred, FL							6.93	
Godsy et al	1992	x		Pensacola, FL							0.87	
Durant et al	1997	x		Unnamed, USA	20	B, T, X, E	x		2-5mg/l		3.5 to 2.3	
Holm et al	1992		x	Vejen, Denmark	22	Phenol		x			635 to 751	
Williams et al	1997	x	x	Anon, USA	10	N	x	x	(~1000ug/l - background) 4mg/l in lab		10 to 50	
Hunkeler et al	1999	x		Toronto	~10	B, T, oX, N	x		~120ug/l each		B = 15; T = 15; X's = 50	
					12-18 field; 25 lab	B, T (+ chlorobenzene)	x	x			50 to 100	
					nq	PCE, TCE, DCE, VC		x	14ppm PCE (+50ppm CH3OH) in microcosms		1 to 2	
											1 to 2	
Davis et al			x	Perth, Australia							3 to 4	
											2 to 3	

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
					nq	BTEX, N			NAPL - <10ug/l along plume C.L. Dissolved conc'ns up to 75ppm, sed conc'ns to 1200mg/kg		>800	
											100 to 120	
											230	
											235	
											170	
Major et al	1991	x		Toronto, Canada							125	
Flyvbjerg	1992	x		Fredensborg, Denmark							33 to 160	
Zipper et al	1998		x	Kolliken, Switzerland	10	PCE, TCE, DCE, VC, acetone, etc.		x	<2mg/l PCE in microcosms		7.5	
Bradley et al		x		Keyport, WA	10, 20	P, T ex-creosote and similar		x	P ~2mg/l; T ~0.2mg/l		7 to 10	More detailed kinetic experients done with isolated mixed cultures low relevance
Davis et al	1994	x		Unnamed	11-16	Mecoprop		x	E mecoprop <1mg/l in groundwater		* Info only *	
Wing	1997		x	Santa Clara, CA	Nq	DCE	x	x	Nq		3 to 10	
Peijnenburg et al		x		Nieuwesluijs, Netherlands	12	B	x		1; 10	mg/kg	75; 46	
Ei et al			x	Dover AFB, Delaware, USA	15	TCA					1059	
					20	1,2-DCA + other haloaliphatics		x	Not explicit. Indicates <20uM		51.5	
					16-19	TCE, DCE, VC; minor DCA, PCE	x	x	0.1-40um; approx 5-10000ug/l in samples		548 to 1789	
											1095 to 4380	
											803 to 3395	

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
Yang et al			x	Various in Wisconsin, Illinois							913 to 1132	
Wilson et al		x	x	St Joseph, MI; Picatinny NJ							1168 to 1241	
Wilson et al	2000	x	x	Elizabeth City, NC, USA	nq	B(TEX, MTBE) - Data for B only			Various		85 to 1390	
Wiedemeier et al		x			10	TCE		x	25mg/l - background		182 to 693	
					19-24	MTBE, BTEX		x	LNAPL - 6/g. Most work in area MTBE 65-610ug/l, B 140-2200 ug/l		72	
						Haloaliphatics					256960	
											0.7m to 1.3m	
											14965	
											43.8	
											22265	
											26280	
											401 to 912	
											51100 to 62050	
											171555 to 138700	
											110 to 292	
											474500000	
											474500000	
Harrison et a		x		Four Ashes							43800000000	
Nielsen et al	1996	x	x	Vejen, Denmark							7.434E+12	
Klecka et al	1990	x		Norman, OK	15	Phenol (+ co-contaminants)	x	x	76-2500mg/l phenol		8.7 to 14.7	
Reinhard et al	1997	x	x	Seal Beach, CA	10	B, T, oX naphth, PLE, TCE, phenol		x	Variable, when poss ~150ug/l		Not determined	Cannot differentiae biotic and sorption effects
					20	1,1,1-TCA (+ other leachate contams)	x	x	0.1 & 0.5mg/l		43 to 210	

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
					Nq	B, T, E, oX, (mX + pX - not resolved)		x	B ~750ug/l; T ~74ug/l; E ~90ug/l X's 16-150ug/l		Unclear	
											19	
											50	
Gieg et al	1999	x	x	Denver, CO							30	
											30	
					nq	BTEX		x	>1000mg/kg sediment - <100mg/kg		50	
											10 to 15	
											25	
											40	
Distefano	1999	x									30	
											40	
Nielsen & Keasling	1999	x		CA site, no details	35	PCE, VC		x	0.35uM - 5uM		2	
Haston & McCarty		x									22	
Anderson & Lovley	1999	x		Bemidji MN, Hanahan SC, Columbus MS	30	TCE		x				
					25	PCE, TCE, DCE, Vc			0-50uM		See sheet	
					nq	Naphthalene, benzene			12uM B		30 to 60	
Nales et al		x		Bottle microcosms 14C							8 to 80	
Ravi et al			x								28	
					20-23	BTEX			150uM B, 50uM each TEX's		See sheet - includes inhibition data	
					nq	1,1-DCA; 1,2-DCA; B		x			575 to 602	
Schirmer et al			x	Borden							486 to 649	
Schilling et al			x	Cedar Rapids, Iowa							937 to 1150	

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
Sinclair et al			x	Patrick AFB, FL	nq	MTBE (BTEX)	x		<3mg/l		577.5	
Daniel & Borden			x	Sampson NC	nq	TCE, DCE, VC		x			TCE 305-723d; DCE 264-408d; VC 199-550d	
					nq	B		x	<1mg/l		34-68	
					nq	BTEX, MTBE	x	x	<10mg/l BTEX; <1mg/l MTBE			
									MTBE		693	
									B		495	
									T		110	
									E		119.4827586	
Hunt et al		x		Pure culture lab study & unnamed site microcosms (Brazil)					mpX		198	
									oX		407.6470588	
					20	BTX & Ethanol	x		BTX <300mg/l, Ethanol <10000mg/l			
									EtOH		1.5	
									T + 100 ppm EtOH		9	
									E + 100 ppm EtOH		9	
Brown et al			x	George AFB, Florida					B + 300 ppm EtOH		7	
									B + 300 ppm EtOH		>40	
					nq	BTEX	x	x	<5mg/l			
									B		196.3172805	
									T		163.8297872	
v d Berg et al			x						E		272.8346457	
Cox et al	2001 (conf)	x	x	Louisiana, USA					X		267.5675676	

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
v d Berg et al			x	Heemstede, NL	16 - 20	PCE, Gasoline, distill'n heavies from dry cleaning solvent recovery			PAH, TPH to 5500ug/l; EX to 2400ug/l, PCE 0 - DNAPL		80-139	
v d Berg et al			x		nq	1,2-DCA	x	x	>50mg/l		Field = 33 - 230d; lab = 1 - 8d	
v d Berg et al			x	Montfort, NL	12 - 18	Primarily PCE< off-site TPH spill		x	<2500ug/l at 3m; <30000ug/l @ depth		51-1000	
Mason et al			x	Lakehurst, NJ	10 - 15	PCE; recovery dist'n heavies; diesel or FO?					PER - cis DCW 0.3 - 5y; PER - ETH 6.5y; highly variable	
					11 - 18	PCE, TCE, BTEX (and other TPH)			4 - 11mg/l DOC		PCE - VC or ETH 1.2 - 3.1y	
					nq	PCE, TCE, DCE, VC	x	x	<200 ug/l			
									PCE Aerobic		>230	
									PCE Anaerobic		1.5	
									TCE Aerobic		21	
									TCE Anaerobic		1.5	
									DCE Aerobic		5.7	
									DCE Anaerobic		1.5	
Stephens & Nelson			x	Arizona					VC Aerobic		0.1	
Cox et al		x		Louisiana					VC Anaerobic		0.1	
					25	TCA			TCA		Abiotic 0.9y	
					20	1,2-DCA	x	x	10 - 1000mg/l 1,2-DCA			
									Aerobic 10mg/l		2 - 5	
Ellis et al		x		Flitwick, UK					Aerobic to 800mg/l		8 - 10	
									Anaerobic all conc'ns		<6 days	

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
					nq	PCE, TCE, DCE, VC	x	x				
									PCE		130	
Hardy et al			x						Aerobic DCE		25	
									Aerobic TCE		25	
					nq	PCE, TCE, DCE		x	PCE ~13mg/l max			
									PCE		<840	
Lee et al		x		SE, USA					TCE		<182	
									DCE		<21	
					22	PCE, TCE, DCE, VC		x	PCE 150mg/l (sat'n)			
									PCE		31	
									TCE		23	
Thomas & Chiampo			x						DCE		77	
									VC		44	
					14	Phenol, T, mpX, oX, E	x	x				
									Phenol		47 - 80	
									T		133 - 473	
									E		76 - 286	
Leethem & Larson			x	Unnamed, Texas					mpX		63 - 322	
Mahaffey et al		x		Aerobic-anaerobic					oX		109 - 217	
					nq	VC	x	x	<10mg/l		400	
					18 - 20	TCA, TCE, 1,1-DCE, DCA	x	x	Not explicit			
									TCA Aerobic		63.23625	
									TCA Anaerobic		31.618125	
									1,1-DCE Aerobic		38.91461538	
									1,1-DCE Anaerobic		42.1575	
									TCE Aerobic		84.315	
									TCE Anaerobic		38.91461538	
Reid et al	1997		x	Florida					DCA Aerobic			
Wilson et al	1997	x		Elizabeth City, NC					DCA Anaerobic		126.4725	

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
Robb & Hayes-Martin	1997		x	Unnamed, NE USA	nq	MTBE, B			nq		B, 48 - 3466 days MTBE, Avg = 597d	
					nq	MTBE		x	0 - 4mg/l		97.09	MTBE alone
					nq	BTEX, TCE	x	x				
Presecan & Friesen			x	Western USA					BTEX		270.1	
Wilson & Cho		x	x	Elizabeth City, NC					TCE		4000	
					7 - 11	Phenol	x	x	Not given in detail; <64mg/l Phenol		897 days	
						MTBE			<2mg/l			
Corsenil et a	2000		x	Brazil					MTBE alone		97.28653846	
									MTBE + 1 BTEX		79.0453125	
					25	Ethanol, BTEX	x					
									Ethanol		602.25	
									B		1487.911765	
									T		616.9390244	
									E		843.15	
Kota et al	1997	x	x	Pender, NC					mpX		3613.5	
									oX		1686.3	
					18 field; 16 lab	BTEX		x	0 - 26mg/l BTEX			
									B field		346.5	
									B microcosm		28.875	
									B insitu microcosm		30-140	
									T field		330	
									T microcosm		15.4	
									T insitu microcosm		No degradation	
									E field		462	
									E microcosm		No degradation	
									E insitu microcosm		No degradation	
									oX field		330	
									oX microcosm		12.375	

Authors	Year	Type		Location	Temp °C	Contaminant	biodegradation					Comments
		Lab	Field				Aerobic	Anaerobic	Concentration	Unit	Half Life ($t^{1/2}$) days	
									oX insitu microcosm		No degradation	
									mpX field		533.0769231	
Morgan et a	1993	x		Uiterburen, NL					mpX microcosm		34.65	
									mpX insitu microcosm		48.46153846	
					15	B	x		18	mg/l	3	
						T	x		1.7	mg/l	3	
						E	x		0.17	mg/l	3	
						oX	x		0.2	mg/l	1.3	
		x				mX + pX	x		0.4	mg/l	14	
						B	x		0.5	mg/l	2	
						B		x	18	mg/l	35	
						T		x	1.7	mg/l	57	
						E		x	0.17	mg/l	170	
						oX		x	0.2	mg/l	No degradation	
						mX + pX		x	0.4	mg/l	103	
						B		x	0.5	mg/l	22	

Authors	Year	Type		Location	Contaminant		Test Type	Aquifer Properties	Physical					
		Lab	Field			Concentration Range (ug/l)			foc (%)	koc (l/kg)	Kd (l/kg)	kow (l/kg)	Retardation Factor	Summary / comments
Ptacek & Gillham	1992	x	x	Borden, Canada	tetrachloroethene	330	column, batch, field	fine grained sand with minor clay	0.02				1.268	PCE, 290cm/d, equ, lab column
													1.846	PCE, 18 cm/day, equ
													1.402	PCE, 290 cm/day, non-equ
													2.648	PCE, 18 cm/day, non-equ
													1.79	PCE, 380cm/d, equ, field
													1.95	PCE, 380cm/d, non-equ, field
													2.02	PCE, 270cm/d, equ, field
Allen King et al	1996	x		US	PCE, TCE	1-90,000 PCE, 1 - 800,000 TCE	Batch	clays, variable foc	0.18-3.83		found to be concentration dependent		variable	very relevant paper
Curtis et al	1986	x	x	Borden	PCE,	1-50	Batch	fine grained sand with minor clay	0.02				2.7-3.9	very relevant paper
Ball & Roberts (1)	1991	x	x	Borden	PCE	0.6 - 46,000	Batch	fine grained sand with minor clay	0.02		0.9			
Piwoni and Banerjee	1989	x		US	PCE, benzene,	up to 15000	Lab		low!					
Binger et al	1999			Canada	PCE	40-100	Batch	poorly sorted glacial deposit and reduced shale	0.54	24060	122			reduced glacial deposit
									0.34	38810	134			reduced glacial deposit
									1.7	9220				shale fragment
									0.18-0.35	2240 - 4470	4-10			shallow oxidised material
Bright et al	2000	x		UK	BTEX, TCE, PCE, naphth, TeCA, TCA	120-676	columns	Quartz sand; 2 x landfill clays (10% in QS)	Sand <0.0073; clays 2.6 - 3.9%					
					Toluene	558		5% clay, 95% sand	clay = 3.9		1.15			
					Toluene	558		10% clay	clay = 3.9		3.28			
					Benzene	385		5% clay, 95% sand	clay = 3.10		0.67			

Authors	Year	Type		Location	Contaminant		Test Type	Aquifer Properties	Physical					
		Lab	Field			Concentration Range (ug/l)			foc (%)	koc (l/kg)	Kd (l/kg)	kow (l/kg)	Retardation Factor	Summary / comments
					Benzene	385		10% clay	clay = 3.11		0.88			
Odutola et al	2000	x			chloroform	2000-8000	batch	karstic limestone	0.002		0.01 - 0.011 and 0.041-0.096			importance of pore size and not assuming sorption is dominated by foc in low foc environments
Benker et al	1998	x	x	Perth, Australia	TCE	300 - 10,000	batch, column, field transport	unconsolidated quaternary sand	0.0013					Various R's, one reference to concentration
Broholm et al	1999	x		Denmark	PAHs not on list	up to solubility limits		clay rich till						complex findings relating to competitive corption and multimolecular sorption
Means et al	1980	x		US	PAHs not on list	-								no comments on effect of concentration
Goerlitz et al	1985	x		Florida	Phenol, naphthalene	-	batch, column	delataic fine to coarse sand depositswith discontinuoussilts/clays	nq					
King and Barker	1999	x	x	Borden	phenol, xylene, naphthalene	>5000	field				0.22, N, .11, X		2.2 N, 1.6, X	
Thierrin et al	1995		x	Perth Western Australia	BTEX, naphthalene	1.2 - 5.2 mg/l	field	fine - medium dune sands	0.08 - 0.6				1.02 (B), 1.04 (T), 1.12(T), 1.32(N)	
Jury et al	1987	x			Parathion					11000				
Lane & Loehr	1995	(4 methods)			naphthalene									comparison of different methods
Bjerg et al	1996	x (batch)	ISM	Denmark	BTEX, naphthalene	100-150		sandy aquifer	low					
											0.05-0.08			B
											0.08-0.13			T
											0.15-0.24			X
											0.4-0.43			N
Angley et al	1992	x			BTEX	up to 5000	model, column	sandy, surficical aquifer	0.015				1.4	B
													1.7	T, EB, o-X
													2	m,p-X

Authors	Year	Type		Location	Contaminant		Test Type	Aquifer Properties	Physical					
		Lab	Field			Concentration Range (ug/l)			foc (%)	koc (l/kg)	Kd (l/kg)	kow (l/kg)	Retardation Factor	Summary / comments
Larson et al	1992	x		Denmark	BTEX, TCE, PCE, B(a)P	effect of DOM up to 300mg/l		low TOC fine to coarse sands	0.016 - 0.034					
Thornton et al	2000	x		UK	BTEX, TCE, PCE, N	120-676	column	sandstones	0.026 - 0.147				various	
O'Brien et al	2000		x	California	MTBE					10 - 12.5				
McCarthy et al	1989	x		US	BaP		batch							affinity of BaP to DOM
Diaz et al	2000				MTBE, Ethanol					10 (MTBE), 15 (Ethanol)				
Abou - Rizk et al		x		USA	Cyanide, phenol		microcosms	Sandy						
Aelion	1996	x		Hanahan, SC	B, T		microcosms	Fine sands, minor clay and silt layers						
Alvarez et al	1994			Unnamed, USA	T			Few data given - Sandy						
Anderson & Lovley	2000		x	Oklahoma	Hydrocarbons - benzene data reported									
Anderson & Lovley	1999	x		Bemidji MN, Hanahan SC, Columbus MS	Naphthalene, benzene		microcosms 14C-label							
Angley et al	1992	x		Lake Alfred, FL	B, T, X, E		microcosms	97% sand						
Baker et al		x		Beaufort, SC	BTEX ex-gasoline spike		microcosms	Sandy	Very low				Very low	
Barlaz et al		x	x	Rocky Point, NC	BTEX		microcosms	Sandy						
Bekins et al		x		Pensacola, FL	Phenol (and related)		microcosms	Sandy 0 - ~5m; sandy clay ~5m - ~10-15m; sandy to 30m+; clay lenses	0.07%				0.07%	
Bjerg et al	1996		x	Vejen, Denmark	B, T, oX, N			Glaciofluvial sand aquifer						
Borden et al	1997	x	x	2 sites, USA	BTEX		microcosms - in situ and lab	SB site : Coarse sand / gravel, RP site silty clays / fine sands	SB site 2.2				SB site 2.2	
Bouwer et al	1998	x		Unnamed	B, T, N		microcosms							
Bradley & Chapelle		x		Cecil Field, FL	DCE, VC		microcosm							
Bradley & Chapelle		x		Cecil Field, FL	DCE, VC		microcosm	Primarily gw - streambed sed samples						Insignificant

Authors	Year	Type		Location	Contaminant		Test Type	Aquifer Properties	Physical					
		Lab	Field			Concentration Range (ug/l)			foc (%)	koc (l/kg)	Kd (l/kg)	kow (l/kg)	Retardation Factor	Summary / comments
Bradley & Chapelle	1996	x		Plattsburgh AFB, NY; Cecil Field, FL	VC		microcosms	No data						
Bradley et al		x		Cecil Field, FL	VC, DCE		microcosms	Streambed seds	2.5wt%				2.5wt%	
Bradley et al		x	x	Plattsburg AFB, NY	VC									
Bradley et al		x		Laurens and Charleston, SC	BTEX, MTBE ex-gasoline		microcosms	Coarse sand (L); silt/clay high OC (Ch)						
Bradley et al		x		Keyport, WA	DCE			Fine-med sands, 0.05-0.1wt% Mn (IV)						
Broholm & Arvin	2000	x		Mansfield, UK	Phenol		microcosm	Sandstone						
Carr et al	2000	x			PCE, TCE, DCE, 1,1,1-TCA			na						Kow: PCE = 3060; TCE = 395; DCE = 94 (at 24deg C) Experimental measurements
Chapelle et al	1996	x	x	Hanahan, SC	B, T		microcosms	Quartz sands/interbedded clay lenses						
Chiang et al	1989	x	x	Unnamed, USA	B, T, X		microcosms	Medium-coarse sands/gravels, silty clay @ 10-15m	<0.08wt%				<0.08wt%	Insignificant
Corsenil & Alvarez	1996	x			Ethanol, B		microcosms	Sandy						
Corsenil et al	1996	x												
Davidson et al		x		4 Sites, USA	Parathion		microcosms, columns	Primarily Agricultural Soils 1) silty clay loam, 2) sandy loam, 3) Sandy clay loam, 4) organic 'muck'	0.5-3.9					
Davis & Carpenter	1990	x		Norman, OK	VC		microcosms	93% sand	0.24%				0.24%	
Davis et al			x	Perth, Australia	BTEX, N			7-12m dune sand over thick clay altard. High Fe zones in capillary zone						See Thierrin et al 1995, 93
Davis et al	1994	x		Unnamed	B		microcosms	Fill-sands-sand + gravel to ~30m						
Deeb et al		x			BTEX, MTBE		pure culture studies	na						
DeWeerd et al	1998	x		Pinellas FL	TCE & DCM			No data but site known to be sandy						
Distefano	1999	x			PCE, VC		Liquid culture, mixed pop'ns	na						
Dupont et al			x	Eielson, Alaska	TCE			60-90m alluvial sands and gravels						
Dupont et al			x	Hill AFB	B, T									
Durant et al	1995	x		Anon, USA	N, B (and other coal gasification components)		microcosms + 14c	0 - 1.5m fill; 1.5 - 6.0m silts; 6 - 9m sand; 9 - 15m silts; 15 - 21m sand and gravel; 21 - 24m dense clay; 24 - 27m sand and gravel; bed rock						
Durant et al	1997	x		Unnamed, USA	N		microcosms	Medium-coarse sands	<0.001				<0.001	

Authors	Year	Type		Location	Contaminant		Test Type	Aquifer Properties	Physical					
		Lab	Field			Concentration Range (ug/l)			foc (%)	koc (l/kg)	Kd (l/kg)	kow (l/kg)	Retardation Factor	Summary / comments
Ealden & Paersch	1999		x	Duisberg, Germany	BTEX			0-1.2m fill; 3-6m loamy sands, 6-28m medium sand & gravel						
Ei et al			x	Dover AFB, Delaware, USA	TCE, DCE, VC; minor DCA, PCE			Glacial outwash; ~15m thick; fine-med silty sands; medium-coarse sand + gravel	<0.001				<0.001	Not stated - known to be very low foc aquifer Rf<1.30
Ellis et al			x	Dover AFB, DE	TCE, PCE, DCE, VC									
Ellis et al	2000		x	Dover AFB	TCE, DCE			Sands-silts; TOC<1%						
Flyvbjerg	1992	x		Fredensborg, Denmark	P, T ex-creosote and similar		stirred reactors	no info - liquid cultures						
Furlong et al			x	Bemidji, MN	N			Sand-gravel						
Ghosh et al		x	x	USA	Cyanides		microcosms, columns	Sand, gravel						
Gieg et al	1999	x	x	Denver, CO	BTEX			Sandy loam						
Godsy et al	1992	x		Pensacola, FL	Phenol		microcosm	nq						
Granger et al	1999	x			Gas condensate (BTEX)			Heterog glacial deposits						
Hanson et al	1999	x		Sediment cores ex-Port Heuneme, CA	MTBE, Ethanol		microcosm, bioaugmented	Sandy to ~7m, then clay a/clude						
Harkness et al	2000	x			TCE, DCE, VC		Columns, bioaugmentation	Fine-Med sand; TOC <0.1%	<0.1%				<0.1%	Rf = 0.0 - 0.3
Harrison et al		x		Four Ashes	Phenol (+ co-contaminants)		microcosms, suspended growth only	None added						
Haston & McCarty		x			PCE, TCE, DCE, Vc		Microcosms							
Holm et al	1992		x	Vejen, Denmark	B, T, oX, N		in situ microcosm	Glaciofluvial sand-gravel						
Holman et al		x			Naphthalene		microcosm/columns feed + draw	Silty loam (17% clay - 34% sand - 48% silt)	0.20%				0.20%	Kp naphthalene, this sediment log Kp = 2.91
Hunkeler et al	1999	x		Toronto	PCE, TCE, DCE, VC		microcosms	Upper clay - sand silt - lower clay (altard)						
Isalon et al		x		na	PCE		columns	Sand packing						
Johnson et al	2000	x		Hampshire, UK	Mecoprop			Chalk (ground for microcosms)						
Jury et al		x		generic	Parathion		na	na						koc = 11 m^3/kg
Kampbell et al	1996		x	Patrick AFB, CA	BTEX			Beach sand to 7.5m; marl						
Kao & Borden		x		4 sites	BTEX		microcosms							
Kaseros et al	2000	x			PCE		column studies	Graded sand	0.1				0.1	
Kazumi et al	1997	x		Various US	B		microcosms	No data						
Kelly et al	1996	x			BTX		columns - quartz sand and inos	Lab packed with Quartz sand	x				x	Insignificant
King et al			x	Borden, Canada	Phenol, X, N									
Kirtland et al	2000		x		Gasoline (UST leak)			0 - 4.6m clayey; 4.6 - 6.7m sandy clay; 6.8 - 10.7m sandy clay loam						Insignificant TOC

Authors	Year	Type		Location	Contaminant		Test Type	Aquifer Properties	Physical					
		Lab	Field			Concentration Range (ug/l)			foc (%)	koc (l/kg)	Kd (l/kg)	kow (l/kg)	Retardation Factor	Summary / comments
Klecka et al	1998	x		3 sites in USA	1,2-DCA		microcosms	Primarily sandy or sand-gravel						
Klecka et al	1990	x		Norman, OK	1,1,1-TCA (+ other leachate contams)			94% alluvial sand/silt/gravel/clay 10-14m, then 100m dense clay						
Kromann et al		x		Demark landfills x 8	TCA, PCE, TCE, DCE, VC		microcosms	Quartz sand and leachate samples						
Leahy & Shreve	2000	x			PCE + leachage organics (~110-220ppm BODs)		liquid microcosms	No packing						
Lemer et al	2000		x	Four Ashes	Phenol and related			See related papers						
MacFarlane et al			x	Baltimore, MD	N, BTEX									
Major et al	1991	x		Toronto, Canada	PCE, TCE, DCE, VC, acetone, etc.		microcosms	Complex layered clays, silts, sands						
Meehan et al		x		2 sites, Australia	Cyanide		columns	Sand						
Nales et al		x		Bottle microcosms 14C	BTEX									
Nielsen & Keasling	1999	x		CA site, no details	TCE		Liquid culture	na						
Nielsen et al	1996	x	x	Vejen, Denmark	B, T, oX naphth, PLE, TCE, phenol		ISM's and microcosms	Unconfined sandy (73-91% coarse sand)						See sheet
Peijnenburg et al		x		Nieuwesluijs, Netherlands	1,2-DCA + other haloaliphatics		microcosms							
Ravi et al			x		1,1-DLA; 1,2-DCA; B			Complex glacial till + o/wash						Rf B = 1.27; DCA's = 1.10 - 1.12
Reinhard et al	1997	x	x	Seal Beach, CA	B, T, E, oX, (mX + pX - not resolved)			Sandy/silty	0.02%				0.02%	Kd Tol = 0.17l/kg
Sims & Abbott		x		USA	napthalene, B(a)P		microcosms	sandy Loam	0.41-2.9				0.41-2.9	95% incorporated into soil Humics
Sorenson et al			x	INEEL, USA - TAN area	PCE, TCE, 1,2-DCE (+ radioisotopes)			Fractured basalt, interbedded sedimentary						
Stauffer et al			x	Columbus MI	BTEX, N			Primarily sand, mixed perm silty layers						
Suflita & Mormile		x		USA (Oklahoma?)	MTBE, Ethanol		microcosms	nq						
Thierrin et al			x	Perth, Australia	BTEX, naphth		Tracer test (2H)	Med - Fine sands 0-12m over >4m clay a/drde	0.08-0.6%				0.08-0.6%	Rf: B = 1.02; T = 1.04; pX = 1.12; N = 1.32
Thierrin et al	1993	x	x	Perth, Australia	BTEX, naphthalene		columns	Sand	0.08-0.6%				0.08-0.6%	Rf (field) B = 1.02; T = 1.05; E = 1.40; X's = 1.12; N = 1.32
Thornton et al	2000	x			B, T, N, TCA, TCE, PCE		Triassic s/stone packed columns	Triassic s/stone (crushed for packing)	0.03 - 0.15%				0.03 - 0.15%	See separate sheet
US DoE			x	Pinellas FL	PCE, TCE, DCE, DCM, VC, Tol		accelerated	Silty sand, <10% clay, <500ppm TOC						
van Aalst, van Leeuwen et al	1997	x		Gromingen, Netherlands	PCE, TCE		columns	Sandy silt 0-8m, 8-12m clay, >12m sand	0.003				0.003	
Weaver et al			x	St Joseph, MI	TCE, DCE, VC									
White & Markwiese	1994	x		New Mexico	Cyanide		columns	Ex-spoil heap	na				na	

Authors	Year	Type		Location	Contaminant		Test Type	Aquifer Properties	Physical					
		Lab	Field			Concentration Range (ug/l)			foc (%)	koc (l/kg)	Kd (l/kg)	kow (l/kg)	Retardation Factor	Summary / comments
Wiedemeier et al			x	Plattsburg AFB, NY	TCE, BTEX, DCE, VC			Sand (fine-med) 0-30m; clay, variable	Very Low				Very Low	Negligible
Wiedemeier et al	1998	x	x	Tibbetts Road, Barrington NH, USA	BTEX, TCE		microcosms	Overburden and bedrock						
Wiedemeier et al		x			Haloaliphatics									
Williams et al	2001		x	Helpston, Lincolnshire	Mecoprop			Oxford clay (up to 33m) then primarily mudstones & limestones to Lincolnshire L/stone* @ 50-60mbgs (* Oolitic above, fine grained sandy below, up to 23m thick)						
Williams et al	1997	x	x	Anon, USA	B, T (+ chlorobenzene)		microcosms	5-9m highly perm unconsol seds underlain by low perm bedrock						
Wilson et al		x	x	Tibbetts Road, Barrington, NH	TCE, B, T		microcosms	Overburden and bedrock aquifers						
Wilson et al		x	x	Traverse City, MI	BT X									
Wilson et al		x	x	St Joseph, MI; Picatinny NJ	TCE		microcosms	Sandy						
Wilson et al	2000	x	x	Elizabeth City, NC, USA	MTBE, BTEX		microcosms	0-3m silty clay; 3-8m silty and fine sand						
Wing	1997		x	Santa Clara, CA	TCA			Silt-silty sand						
Yager et al		x		Niagara, NY	TCE, DCE		microcosms	Thin fractured bedded dolomite incl thin bituminous material						
Yang et al			x	Various in Wisconsin, Illinois	B(TEX, MTBE) - Data for B only			See sheet						
Zipper et al	1998		x	Kolliken, Switzerland	Mecoprop			Fractured marls, interlayed sandstone banks	Very low				Very low	NSD between (S-) + (R) - mecoprop: minimal oc, sorption to minerals only. Kd ~ 10 -4 l/m2

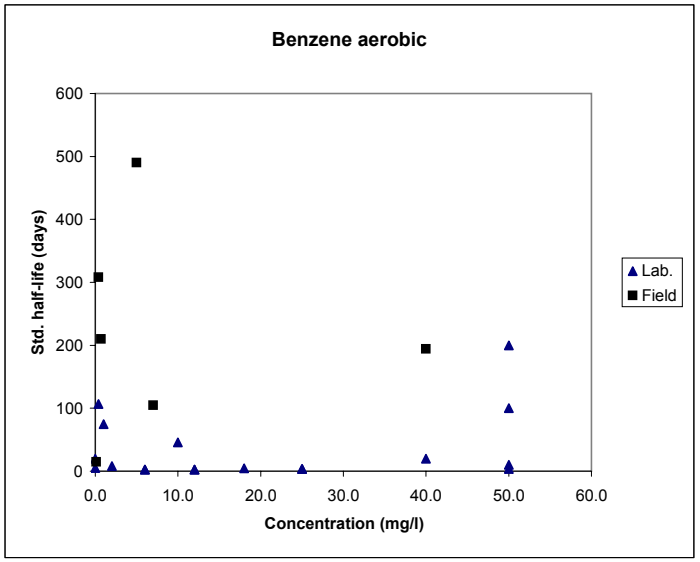
APPENDIX 7

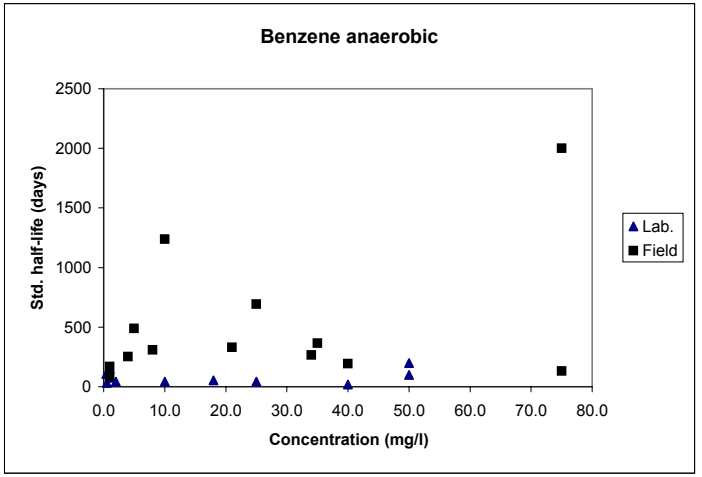
Biodegradation data summary sheets

Biodegradation data summary sheets

Benzene

Conditions	Lab./field	Country	Temp. (deg. C)	Concentration (mg/l)	Half-life (days)	Temp correction factor	Standardised half-life (days)
Aerobic	l	USA	10	0.4	107	1.0	107
	l	USA	nq	40.0	10	2.0	20
	l	USA	22	50.0	50	2.0	100
	l	USA	22	50.0	100	2.0	200
	l	USA	10	0.0	5	1.0	5
	l	USA	10	0.0	20	1.0	20
	l	USA	20	2.0	4	2.0	8
	l	USA	12	1.0	75	1.0	75
	l	UK	25	6.0	1	2.5	3
	l	UK	25	12.0	1	2.5	3
	l	UK	25	25.0	2	2.5	4
	l	UK	25	50.0	4	2.5	10
	l	UK	25	6.0	1	2.5	3
	l	UK	25	12.0	1	2.5	3
	l	UK	25	25.0	2	2.5	4
	l	UK	25	50.0	2	2.5	4
	l	USA	12	10.0	46	1.0	46
	l	Netherlands	15	18.0	3	1.5	5
	f	USA	10	0.4	308	1.0	308
	f	USA	nq	40.0	97	2.0	194
	f	USA	nq	0.7	105	2.0	210
	f	USA	nq	7.0	105	1.0	105
	f	Denmark	10	0.1	15	1.0	15
	f	USA	25	5.0	196	2.5	490
Anaerobic	l	USA	16	2.0	28	1.5	42
	l	USA	10	0.4	107	1.0	107
	l	USA	16	10.0	29	1.5	44
	l	USA	22	50.0	50	2.0	100
	l	USA	22	50.0	100	2.0	200
	l	USA	nq	40.0	10	2.0	20
	l	USA	25	1.0	30	2.5	75
	l	USA	25	1.0	60	2.5	150
	l	USA	16	25.0	29	1.5	44
	l	Netherlands	15	18.0	35	1.5	53
	l	USA	15	0.5	22	1.5	33
	f	USA	16	4.0	169	1.5	254
	f	USA	nq	40.0	97	2.0	194
	f	USA	10	8.0	308	1.0	308
	f	Australia	25	75.0	800	2.5	2000
	f	UK	12	75.0	131	1.0	131
	f	UK	12	35.0	365	1.0	365
	f	UK	12	34.0	267	1.0	267
	f	UK	12	21.0	330	1.0	330
	f	USA	25	1.0	34	2.5	85
	f	USA	25	1.0	68	2.5	170
	f	USA	25	10.0	495	2.5	1238
	f	USA	25	5.0	196	2.5	490
	f	USA	18	25.0	346	2.0	692

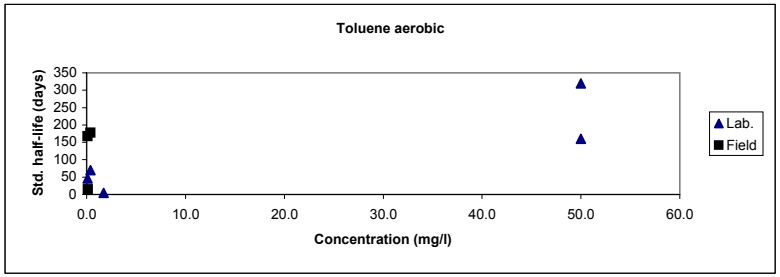


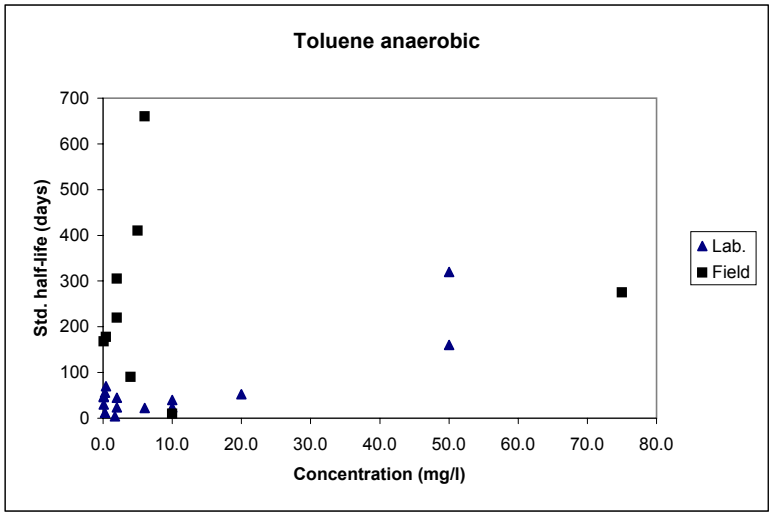


Biodegradation data summary sheets

Toluene

Conditions	Lab./field	Country	Temp. (deg. C)	Concentration (mg/l)	Half-life (days)	Temp correction factor	Standardised half-life (days)
Aerobic	l	USA	10	0.4	70	1.0	70
	l	USA	22	50.0	80	2.0	160
	l	USA	22	50.0	160	2.0	320
	l	USA	?	0.1	23	2.0	46
	l	Netherlands	15	1.7	3	1.5	5
	f	USA	10	0.4	178	1.0	178
	f	USA	?	0.1	84	2.0	168
	f	USA	10	0.1	15	1.0	15
Anaerobic	l	USA	16	2.0	16	1.5	24
	l	USA	16	2.0	30	1.5	45
	l	USA	10	0.4	70	1.0	70
	l	USA	16	10.0	16	1.5	24
	l	Australia	25	10.0	16	2.5	40
	l	UK	18	0.3	6	2.0	12
	l	UK	18	0.3	28	2.0	56
	l	USA	25	20.0	21	2.5	53
	l	USA	22	50.0	80	2.0	160
	l	USA	22	50.0	160	2.0	320
	l	USA	25	0.1	19	2.5	48
	l	USA	25	0.1	12	2.5	30
	l	USA	16	6.0	15	1.5	23
	l	Netherlands	15	1.7	3	1.5	5
	l	USA	?	0.1	23	2.0	46
	f	USA	10	0.4	178	1.0	178
	f	USA	25	10.0	4	2.5	10
	f	USA	10	2.0	305	1.0	305
	f	USA	?	0.1	84	2.0	168
	f	USA	25	75.0	110	2.5	275
	f	USA	?	2.0	110	2.0	220
	f	USA	25	5.0	164	2.5	410
	f	USA	18	6.0	330	2.0	660
	f	USA	16	4.0	60	1.5	90

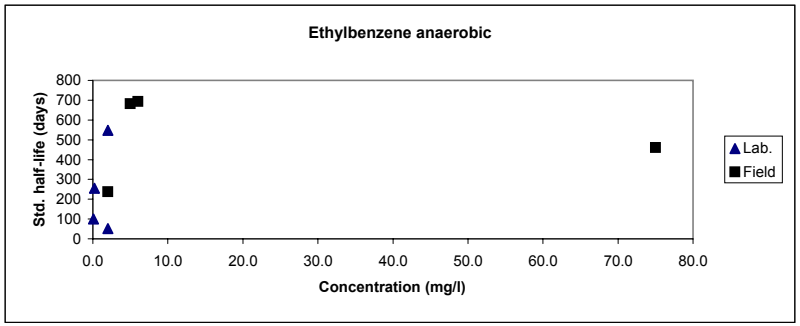




Biodegradation data summary sheets

Ethylbenzene

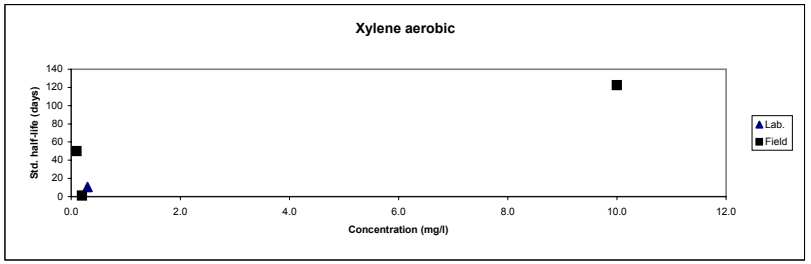
Conditions	Lab./field	Country	Temp. (deg. C)	Concentration (mg/l)	Half-life (days)	Temp correction factor	Standardised half-life (days)
Anaerobic	l	USA	16	2.0	35	1.5	53
	l	USA	16	2.0	365	1.5	548
	l	USA	20	0.1	50	2.0	100
	l	Netherlands	15	0.2	170	1.5	255
	f	Australia	?	75.0	230	2.0	460
	f	USA	20	2.0	119	2.0	238
	f	USA	25	5.0	273	2.5	683
	f	USA	18	6.0	462	1.5	693

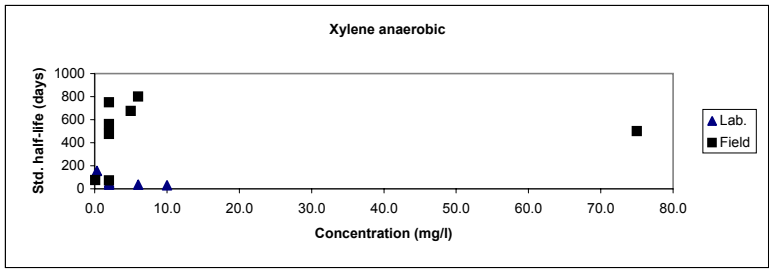


Biodegradation data summary sheets

Xylenes

Conditions	Lab./field	Country	Temp. (deg. C)	Concentration (mg/l)	Half-life (days)	Temp correction factor	Standardised half-life (days)
Aerobic	l	Netherlands	15	0.3	7	1.5	11
	f	USA	25	10.0	49	2.5	123
	f	Denmark	10	0.2	1	1.0	1
	f	Denmark	10	0.1	50	1.0	50
Anaerobic	l	USA	16	2.0	35	1.5	53
	l	USA	16	2.0	25	1.5	38
	l	USA	25	10.0	12	2.5	30
	l	USA	16	6.0	25	1.5	38
	l	Netherlands	15	0.3	103	1.5	155
	f	USA	16	2.0	48	1.5	72
	f	Australia	23	2.0	225	2.5	563
	f	USA	23	2.0	190	2.5	475
	f	USA	25	75.0	200	2.5	500
	f	USA	25	0.1	30	2.5	75
	f	USA	25	2.0	300	2.5	750
	f	USA	25	5.0	270	2.5	675
	f	USA	18	6.0	400	2.0	800

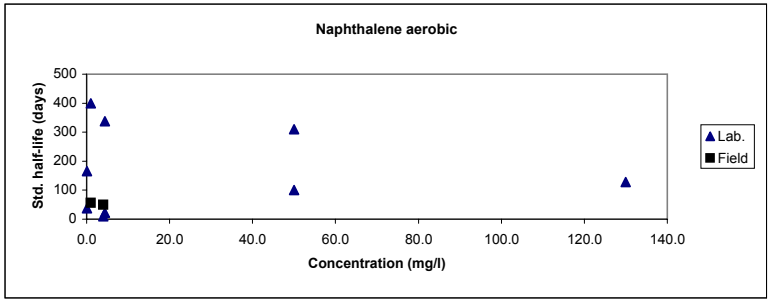




Biodegradation data summary sheets

Naphthalene

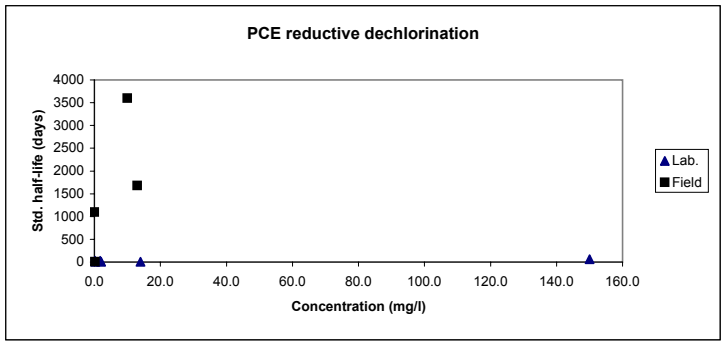
Conditions	Lab./field	Country	Temp. (deg. C)	Concentration (mg/l)	Half-life (days)	Temp correction factor	Standardised half-life (days)
Aerobic	l	Australia	25	1.0	160	2.5	400
	l	USA	22	4.4	11	2.0	22
	l	USA	22	4.4	169	2.0	338
	l	UK	20	0.1	83	2.0	166
	l	UK	20	0.1	19	2.0	38
	l	USA	21	130.0	64	2.0	128
	l	USA	22	50.0	50	2.0	100
	l	USA	22	50.0	155	2.0	310
	l	USA	10	4.0	10	1.0	10
	l	USA	10	4.0	50	1.0	50
	l	USA	?	1.0	28	2.0	56



Biodegradation data summary sheets

PCE

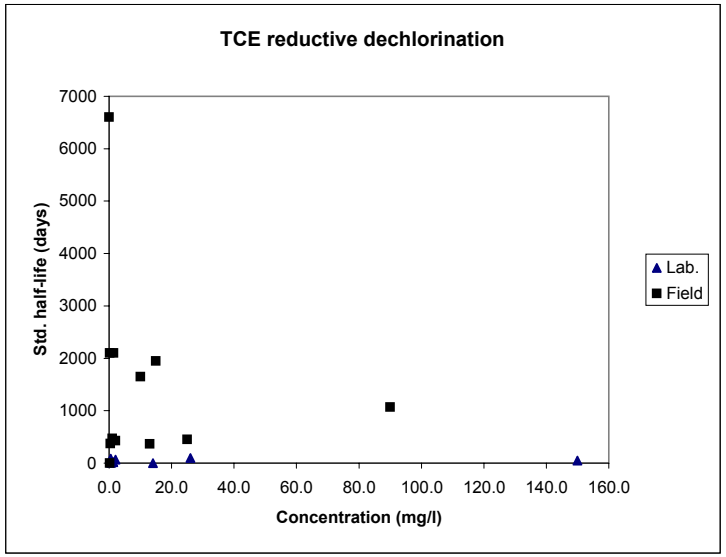
Conditions	Lab./field	Country	Temp. (deg. C)	Concentration (mg/l)	Half-life (days)	Temp correction factor	Standardised half-life (days)
Anaerobic reductive dechlorination	l	UK	18	0.2	14	2.0	28
	l	USA	20	1.7	15	2.0	30
	l	USA	35	0.3	2	4.0	8
	l	USA	22	150.0	31	2.0	62
	l	USA	?	14.0	2	2.0	4
	l	Canada	10	2.0	8	1.0	8
	f	USA	18	0.0	550	2.0	1100
	f	USA	18	10.0	1800	2.0	3600
	f	USA	20	0.2	2	2.0	4
	f	USA	?	13.0	840	2.0	1680



Biodegradation data summary sheets

TCE

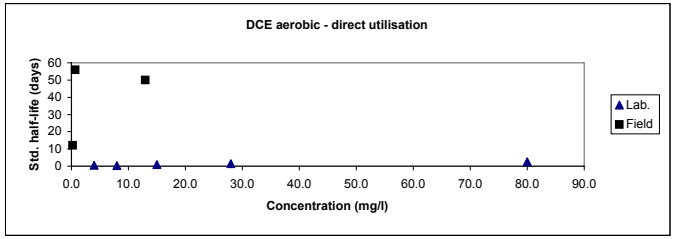
Conditions	Lab./field	Country	Temp. (deg. C)	Concentration (mg/l)	Half-life (days)	Temp correction factor	Standardised half-life (days)
Anaerobic reductive dechlorination	l	USA	10	2.0	70	1.0	70
	l	USA	15	26.0	66	1.5	99
	l	UK	18	0.6	8	2.0	16
	l	UK	18	0.6	4	2.0	8
	l	USA	20	1.3	8	2.0	16
	l	Canada	15	14.0	2	1.5	3
	l	USA	35	0.5	22	4.0	88
	l	USA	22	150.0	23	2.0	46
	f		25	1.4	840	2.5	2100
	f		25	0.4	150	2.5	375
	f		25	0.2	840	2.5	2100
	f		17	15.0	1300	1.5	1950
	f		10	90.0	1066	1.0	1066
	f		10	1.0	468	1.0	468
	f		17	0.0	4400	1.5	6600
	f		17	10.0	1100	1.5	1650
	f		10	25.0	450	1.0	450
	f		20	0.2	2	2.0	3
	f		20	13.0	182	2.0	364
	f		10	2.0	430	1.0	430

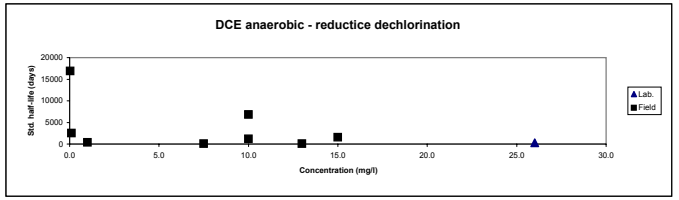


Biodegradation data summary sheets

DCE

Conditions	Lab./field	Country	Temp. (deg. C)	Concentration (mg/l)	Half-life (days)	Temp correction factor	Standardised half-life (days)
Aerobic - direct utilisation	l	USA	20	4.0	0	2.0	1
	l	USA	20	8.0	0	2.0	0
	l	USA	20	15.0	0	2.0	1
	l	USA	20	28.0	1	2.0	2
	l	USA	20	80.0	1	2.0	3
	f	USA	20	0.7	28	2.0	56
	f	USA	?	0.2	6	2.0	12
	f	UK	?	13.0	25	2.0	50
Anaerobic - direct utilisation	f	USA	?	0.1	3614	2.0	7228
Anaerobic - reductive dechlorination	l	USA	?	26.0	140	2.0	280
	f	USA	?	15.0	766	2.0	1532
	f	USA	16	10.0	800	1.5	1200
	f	USA	?	10.0	3390	2.0	6780
	f	UK	?	13.0	21	2.0	42
	f	USA	?	0.1	1265	2.0	2530
	f	USA	?	1.0	169	2.0	338
	f	USA	?	7.5	28	2.0	56
	f	USA	?	0.0	8432	2.0	16863

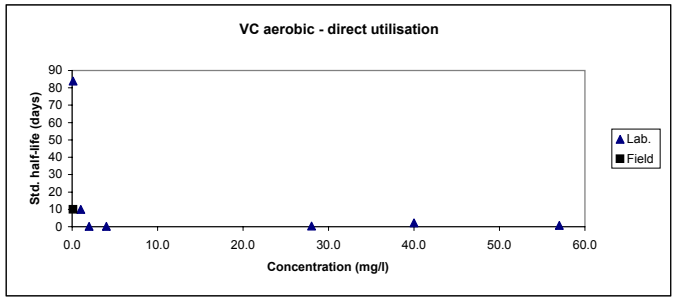


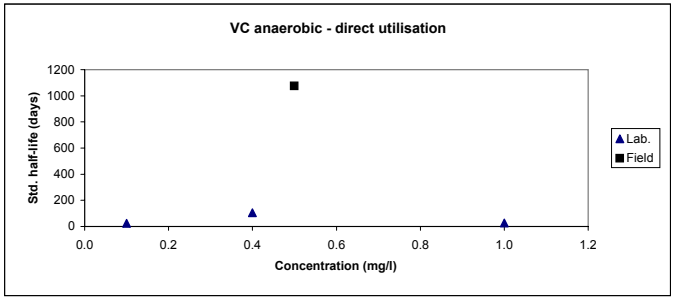


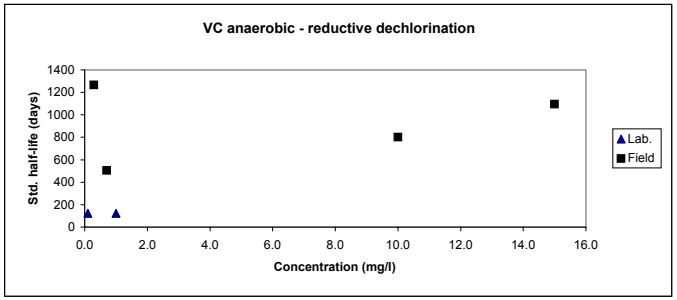
Biodegradation data summary sheets

Vinyl chloride

Conditions	Lab./field	Country	Temp. (deg. C)	Concentration (mg/l)	Half-life (days)	Temp correction factor	Standardised half-life (days)
Aerobic - direct utilisation	l	USA	?	0.1	42	2.0	84
	l	USA	?	2.0	0	2.0	0
	l	USA	?	4.0	0	2.0	0
	l	USA	?	28.0	0	2.0	0
	l	USA	?	40.0	1	2.0	2
	l	USA	?	57.0	0	2.0	1
	l	USA	?	1.0	5	2.0	10
	f	USA	20	0.1	5	2.0	10
Anaerobic - direct utilisation	l	USA	20	0.1	12	2.0	24
	l	USA	?	0.4	53	2.0	106
	l	USA	?	1.0	13	2.0	26
	f	USA	?	0.5	538	2.0	1076
Anaerobic - reductive dechlorination	l	USA	?	0.1	62	2.0	124
	l	USA	?	1.0	62	2.0	124
	f	USA	?	0.7	253	2.0	506
	f	USA	?	0.3	632	2.0	1265
	f	USA	16	15.0	730	1.5	1095
	f	USA	?	10.0	400	2.0	800



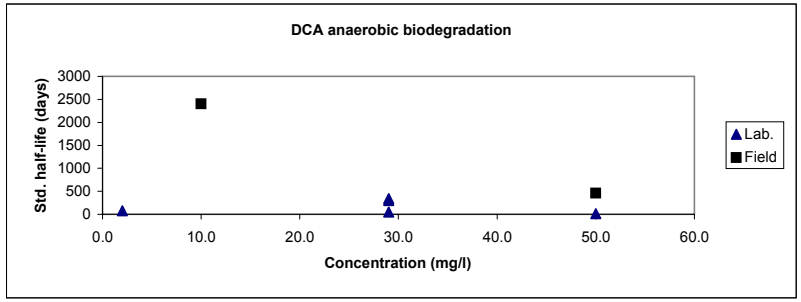




Biodegradation data summary sheets

DCA (both isomers)

Conditions	Lab./field	Country	Temp. (deg. C)	Concentration (mg/l)	Half-life (days)	Temp correction factor	Standardised half-life (days)
Anaerobic	l	USA	20	29.0	25	2.0	50
	l	USA	20	29.0	150	2.0	300
	l	USA	20	29.0	170	2.0	340
	l	Netherlands	15	2.0	52	1.5	78
	l	USA	?	50.0	8	2.0	16
	f	USA	?	10.0	1200	2.0	2400
	f	USA	?	50.0	230	2.0	460



APPENDIX 8

UK site data from unpublished sources

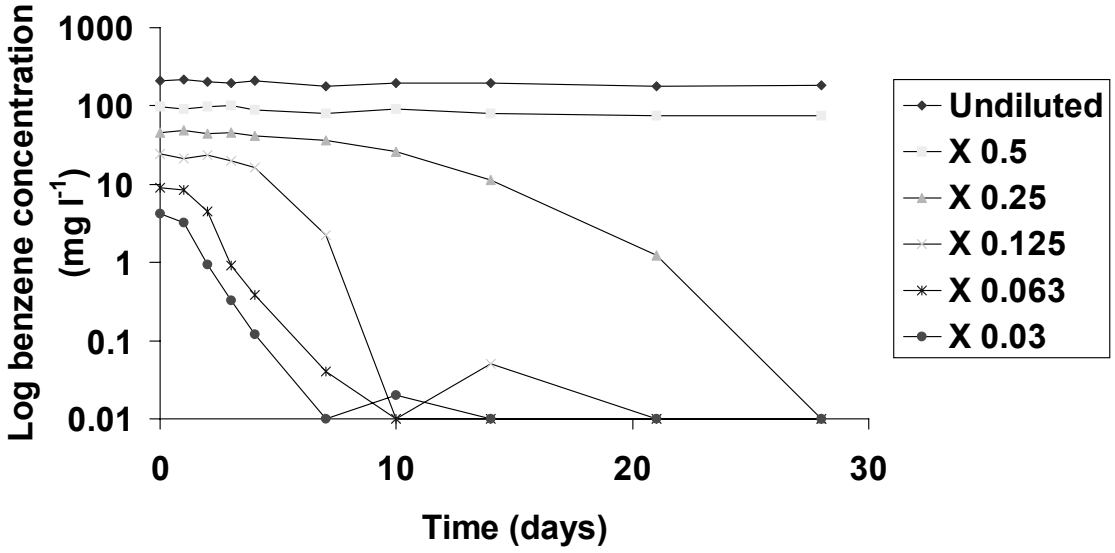
1. Benzene release, oil refinery

A microcosm study was made of aquifer sediment (medium-fine sand) collected from the release area to determine the effects of benzene concentration on aerobic biodegradation rate. Various dilutions of the same material were made to give a range of initial benzene concentrations in the microcosms ranging from 200 mg l^{-1} down to approximately 6 mg l^{-1}. Care was taken in experimental design to provide sufficient oxygen to support aerobic biodegradation and to ensure that adequate nitrogen and phosphorus were present. Incubation temperature was 25ºC.

The results are illustrated in Figure A6.1. It is evident that no significant biodegradation took place at initial benzene concentrations of 100 mg/l or greater. At starting concentrations of 50 mg/l and below, benzene biodegradation took place following a lag period whose duration was proportional to the initial concentration. Approximate half-lives of benzene at these starting concentrations were:

Initial benzene concentration (mg l^{-1})	Benzene half-life (days)
50	4.0
25	1.5
12	1.0
6	<1.0

Figure A6.1. Effect of concentration on benzene biodegradation in laboratory microcosms of aquifer sediments from a spill site. The graph shows the concentration of benzene (logarithmic scale) as a function of time for a series of sediment sample dilutions.



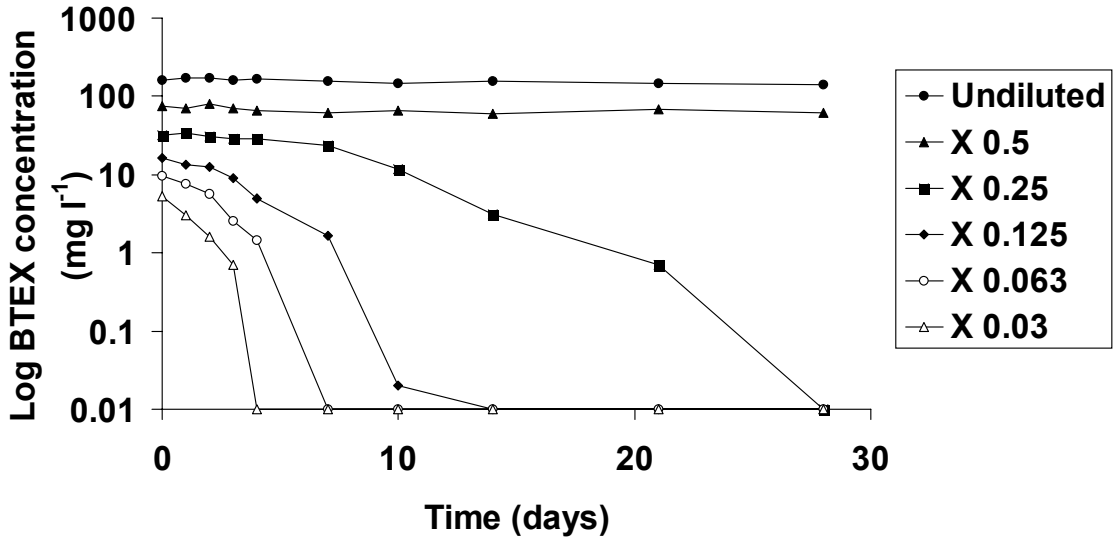
2. Gasoline release, distribution terminal

A microcosm study was made of aquifer sediment (weathered oil shale (blaes)) collected from the release area to determine the effects of total BTEX concentration on aerobic biodegradation rate. Various dilutions of the same material were made to give a range of initial BTEX concentrations in the microcosms ranging from 200 mg/l down to approximately 6 mg l^{-1}. Care was taken in experimental design to provide sufficient oxygen to support aerobic biodegradation and to ensure that adequate nitrogen and phosphorus were present. Incubation temperature was 25ºC.

The results are illustrated in Figure A6.2. It is evident that no significant biodegradation took place at initial BTEX concentrations of 100 mg l^{-1} or greater. At starting concentrations of 50 mg l^{-1} and below, BTEX biodegradation took place following a lag period whose duration was proportional to the initial concentration. Approximate half-lives of BTEX at these starting concentrations were:

Initial BTEX concentration (mg l^{-1})	BTEX half-life (days)
50	1.5
25	1.5
12	1.0
6	<1.0

Figure A6.2. Effect of concentration on BTEX biodegradation in laboratory microcosms of aquifer sediments from an oil distribution terminal. The graph shows the concentration of BTEX (logarithmic scale) as a function of time for a series of sediment sample dilutions.



3. Benzole release, distribution terminal

This site was discussed as Case Study 2 of Appendix 7 to Environment Agency (2000a) and demonstrates the effective MNA of benzene contamination under anaerobic sulphate-reducing conditions. For full details of the background to the data, the case study description should be consulted.

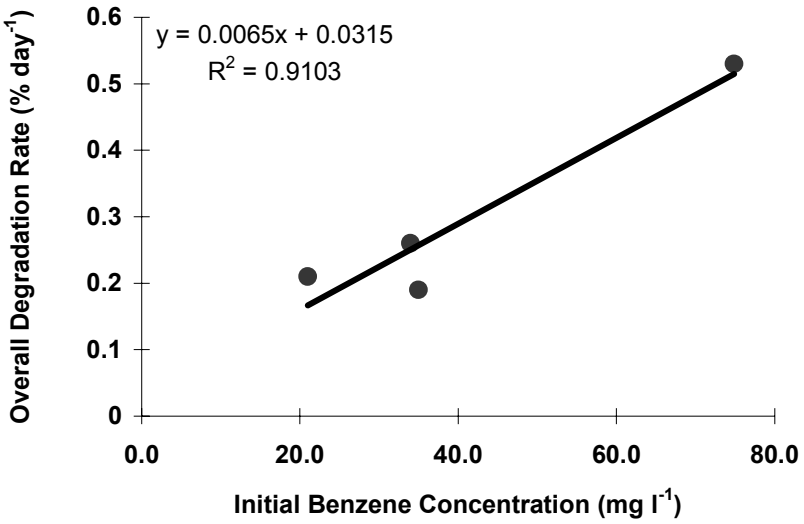
The site was a fuel storage and distribution terminal which was constructed in 1958 and closed in 1991. In the late 1960's an accidental release of the gasoline additive "benzole" (essentially a mixture of benzene and toluene) resulted in contamination of the Whitchurch Sand formation underlying the site. This is a multilayered sand aquifer, which is classified as a "Minor Aquifer" by the Environment Agency and considered unsuitable for economic development but does discharge to surface water. The groundwater across the site is generally encountered at 2.75 to 3.5 m below ground surface and groundwater flows to the southwest. Hydraulic gradient varies across the site from 0.003-0.009. Limited testing suggests that the hydraulic conductivity ranges from 7-14 m day^{-1}.

Evaluation of MNA at the site during the mid- to late-1990's demonstrated that benzene was the only significant contaminant remaining from the original release and that this plume was shrinking as a result of natural attenuation. It was shown that by far the most significant attenuation mechanism was anaerobic biodegradation under sulphate-reducing conditions. Monitoring over a number of years confirmed that natural attenuation was indeed protective of human health and the environment.

For the purposes of this current report, further field data were provided to analyse the rate of benzene biodegradation in the field at different starting concentrations. The results are summarised in the following table and illustrated graphically in Figure A6.3:

Borehole I.D.	Initial benzene concentration ($mg\ l^{-1}$)	Biodegradation rate (day^{-1})	Biodegradation half-life (days)
2-D	74.9	0.0053	131
11	35.0	0.0019	365
F-D	34.0	0.0026	267
K	21.0	0.0021	330

Figure A.3. Effect of initial benzene concentration on field biodegradation rate measured at the benzole release site.



4. Phenol Contamination

This site was discussed as Case Study 1 of Appendix 7 to Environment Agency (2000a) and demonstrates evaluation of the natural attenuation of phenol, cresols and related compounds in the Triassic Sandstone, classified as a "Major Aquifer" by the Environment Agency.

For the purposes of this current report, further laboratory microcosm data were provided on the rate of phenol biodegradation at different contaminant concentrations under various anaerobic conditions:

Contaminants	Anaerobic conditions	Initial phenol concentration (mg l^{-1})	Phenol biodegradation rate (mg l^{-1} day^{-1})	Phenol half-life (days)
PHENOL ALONE	Denitrifying	96.0	0.259	185
	Sulphate-reducing	78.0	0.271	144
	Methanogenic	20.7	0.138	75
Phenol (+ cresols at 14.3 mg l^{-1})	Denitrifying	16.0	0.208	38
Phenol (+ cresols at 7.6 mg l^{-1})	Sulphate-reducing	10.9	0.136	40

It should be noted that there was no evidence of biodegradation being inhibited at the highest initial concentration detected (75 mg l^{-1}).