

Attenuation of mecoprop in the subsurface

Environment Agency Science Group: Air, Land & Water

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Statement of use:

This report presents a literature review of mecoprop attenuation processes in the subsurface environment. It includes summarised rates for biodegradation and sorption reactions from field and laboratory experiments. The presented data may be used for initial risk-screening, but site-specific data collection is expected where the output from an initial assessment of pollution risks indicates that it is sensitive to mecoprop attenuation parameters.

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EXECUTIVE SUMMARY

Mecoprop (MCPP; (RS)2-(2-methyl-4-chlorophenoxy)-propionic acid) is a herbicide that is widely used for agricultural, horticultural and domestic purposes. It is frequently present in landfill leachate and is considered one of the key indicators of pollution from municipal solid waste landfill. It is often selected for consideration within the landfill risk assessment process because it is commonly found in leachate, relatively mobile, and falls within List I of the Groundwater Regulations 1998 (as an organohalogen compound). Information and data to underpin the assessment of mecoprop fate and attenuation in the subsurface is therefore of particular importance.

Mecoprop is water-soluble and subject to relatively little retardation by sorption processes. It is therefore subject to relatively rapid transport in soil pore water and groundwater. A literature review has provided a moderate amount of data on mecoprop sorption under UK subsurface conditions and enabled the development of recommended K_{OC} values (probabilistic range) for use in risk assessments.

Biodegradation of mecoprop is the only significant destructive attenuation mechanism operating under subsurface conditions. Biodegradation in topsoil has been relatively widely studied and is commonly observed, but there is a very rapid decrease in degradation rate with increasing depth through the soil profile, especially at >1 m below ground level (bgl). The potential for biodegradation is seen to vary significantly between sites where mecoprop is applied at typical agricultural use rates, and those sites where mecoprop emissions represents a point source of pollution. Degradation of relatively low concentration 'diffuse' sources is often rapid in shallow aerobic soils, whilst higher concentration 'point sources' are reported to be much less amenable to biodegradation, particularly where the pollutants are present below the topsoil.

The scientific literature on mecoprop biodegradation below the topsoil is limited, and indicates great variability as to whether biodegradation actually takes place and the rate at which it occurs. This lack of consistent information has made it impossible to develop generic guidance on degradation rates to be applied in risk assessments for mecoprop in subsoil, unsaturated subsurface rock formations and groundwater in the UK. The Environment Agency therefore recommends that considerable caution should be applied in applying biodegradation as an attenuation mechanism for mecoprop in the unsaturated subsoil (>1 m bgl) and groundwater components of an initial risk assessment (risk-screening). As a conservative approach, it may be appropriate to exclude biodegradation from risk estimation, unless there is site-specific evidence to support this as an attenuation mechanism.

KEYWORDS:

Natural attenuation, sorption, retardation, biodegradation, herbicides, mecoprop, groundwater, risk assessment, subsurface, aquifer.

1 INTRODUCTION

Mecoprop (2-(2-methyl-4-chlorophenoxy)-propionic acid; MCPP) is a herbicide widely used for agricultural, horticultural and domestic purposes. It is frequently present in landfill leachate and was detected in 98% of UK leachates sampled by Knox *et al.* (2000). Mecoprop is considered one of the key indicators of pollution from landfill (Environment Agency, 2003) and is often selected for consideration within the risk assessment process because it is commonly found, relatively mobile, and a List I substance under the Groundwater Regulations 1998.

Research has been performed on mecoprop contamination arising from landfills, contaminated land sites and approved applications, including investigations of the potential for natural attenuation. Mecoprop is known to undergo attenuation in the subsurface, and has been shown to be both retarded (principally by sorption to organic matter) and biologically degraded in certain redox environments.

This report presents the results of a detailed literature review, which brings together findings and data on the attenuation of mecoprop in soil and groundwater. Conclusions are drawn to provide guidance on the potential for, and magnitude of, mecoprop attenuation in unsaturated subsoil and groundwater under UK conditions. The report provides Environment Agency officers and others with reasonable estimates of the rate of mecoprop attenuation in soil and groundwater under representative conditions. It may be applicable during the assessment of pollution risks from landfills and potentially contaminated land. The Agency will expect site-specific data to be obtained where hazardous activities are proposed in sensitive hydrogeological environments; however, the guidance may be applied for the initial phases of risk assessment (risk-screening), where site-specific information is not available.

The literature search was undertaken using internet data sources, literature abstracting services and by communication with academic groups active in the field of mecoprop research. The literature search procedure is described in Appendix 1. Further information on literature references containing relevant information on mecoprop attenuation is provided in Appendix 2.

2 CHARACTERISTICS AND OCCURRENCE OF MECOPROP

Mecoprop is the British Standards Institute (BSI)-approved and trade name for (RS)2-(2-methyl-4-chlorophenoxy)-propionic acid, also known as MCPP. It is one of a group of chlorophenoxyalkanoic or phenoxy acids and has been in widespread use as a herbicide since the 1960's.

2.1 Chemistry

The chemical structure of mecoprop is shown in Figure 1. As a carboxylic acid, the molecule will be ionised at neutral and alkaline pH values.

The presence of an asymmetric (chiral) carbon atom in the aliphatic side chain results in two different optically active forms (stereoisomers or enantiomers), the R-isomer and the S-isomer (Williams *et al.*, 2003). The pesticide 'Mecoprop' comprises equal proportions of the R- and S-isomers (known as a racemic mixture). However, only the R-isomer has herbicidal properties (Tomlin, 1997), and the product 'Mecoprop-P' has been developed containing only the R-isomer. In this report, the term mecoprop includes both Mecoprop and Mecoprop-P unless otherwise specified.

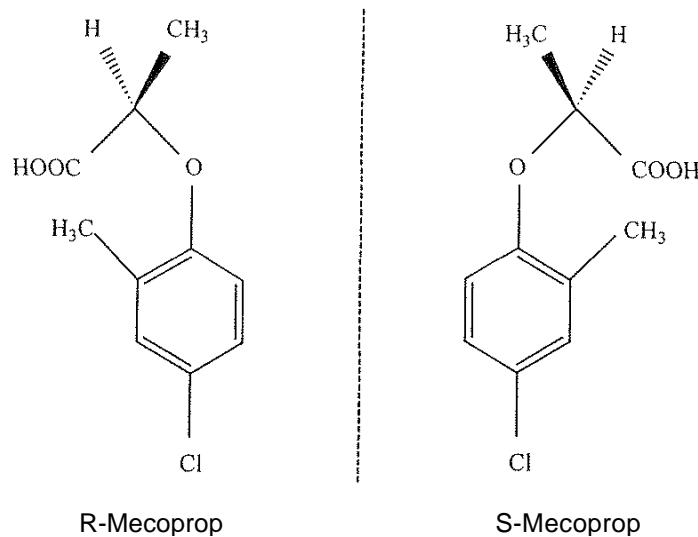


Figure 1. Molecular structure of mecoprop, showing the two enantiomers (after Williams et al., 2003)

2.2 Physico-chemical properties

A compendium of the physico-chemical properties of Mecoprop according to a variety of sources is summarised in Table 2.1.

Table 2.1 Physico-chemical properties of mecoprop (MCPP), from published sources

Parameter	Value	References
CAS no.	000093-65-2 7085-19-0 (acid) 1929-86-8 (potassium salt) 1432-14-0 (diethanolamine salt) 28473-03-2 (isooctyl ester)	
Empirical formula	$C_{10}H_{11}ClO_3$	
Physical state	Odourless white to light brown crystalline solid	
Molecular weight	214.65	
Density / specific gravity	1.28 g/ml at 0°C 0.6 g/ml dry uncompressed	2 2
Vapour pressure	0.31 mPa at 20°C 7.50×10^{-7} mm Hg at 20°C	1, 3, 4 6
Henry's Law constant	1.82×10^{-8} atm.m ³ /mol	6
Solubility in water (mecoprop acid)	734 mg/l at 25°C 620 mg/l at 20°C	1 2, 3, 6
Solubility in water (ammonium salt) (sodium) (diethylamine salt) (dimethylamine salt) (potassium)	320 g/l at 0°C 500 g/l at 20°C 560 g/l at 20°C 660 g/l at 20°C 920 g/l at 20°C	5 5 5 5 5
Octanol - water partition coefficient, K _{ow}	1.26 (pH 7) ($\log K_{ow} = 0.1004$) 871, 1349 ($\log K_{ow} = 2.94, 3.13$)	1, 4 6
Carbon – water partition coefficient, K _{oc}	12 – 25 (dimensionless)	1
Dissociation constant, pK _a	3.78 (20 to 25°C) 3.11 3.1, 3.20, 3.38 at 60°C, 3.75 3.10 (24°C)	1 3 5 6

References:

- 1 Tomlin, 1997, Pesticide Manual
- 2 Department of the Environment (1994a)
- 3 US Agricultural Service pesticide properties database (www.arsusda.gov)
- 4 EXTOXNET (<http://ace.orst.edu/info/extoxnet/ghindex.html>)
- 5 TOXNET (<http://toxnet.nlm.nih.gov/>)
- 6 Howard & Meylan, 1997. Handbook of physical properties of organic chemicals.

The high dissociation constant (pK_a) indicates that the mecoprop acid molecule will be mostly ionised (i.e., negatively charged) in solution at pH values greater than approximately 3.5.

2.3 Mecoprop history and use

Mecoprop was first identified as a herbicide in 1953 (Tomlin, 1997) and introduced commercially in 1956 (Smith, 1989). Mecoprop-P was introduced commercially in 1987. The Department of the Environment (1994a) recommended that Mecoprop should be gradually phased out in favour of Mecoprop-P.

Mecoprop and Mecoprop-P are widely used in agriculture as post-emergence herbicides used to control broad-leaved weeds in cereals and grassland, with applications normally made in the spring and early summer, and also in the autumn. They are used in horticulture for the control of weeds under top fruit crops and for weed control in turf, and by amateur gardeners for weed control in lawns, usually in formulated mixtures and often with added fertiliser. According to Department of the Environment (1994a), mecoprop was the fourth most widely used pesticide active ingredient used on arable crops in England and Wales in 1990; an annual application rate

in the UK of 4000 tonnes was reported for 1988 (Davis *et al.*, 1990). Department of the Environment (1994a) also reported a decline in use of Mecoprop in favour of Mecoprop-P. Herbicide formulations contain mecoprop in the acid form, or as salts (potassium, dimethylamine, diethanolamine, sodium, magnesium) or esters (iso-octyl or 2-ethylhexyl) (Department of the Environment, 1994a). Mecoprop-P is present in pesticide formulations as the acid or as the potassium or dimethylamine salts (Department of the Environment, 1994b). According to Fletcher *et al.* (1995), mecoprop is most commonly applied in the UK in formulations as a salt.

According to Bucheli *et al.* (1998), in Switzerland, mecoprop is also found in the run-off from flat roofs that have been treated with the treatment agent 'Preventol B2', which is a bi-ester of mecoprop. In the Greifensee catchment of Switzerland a field study suggested that the contribution of the mecoprop load to surface waters from flat roofs was of the same order of magnitude as the load from agricultural applications. No studies have been identified investigating the occurrence of mecoprop from similar sources in the UK.

Mecoprop concentrations in drinking water in the European Union are controlled under the 1980 EC Directive on drinking water (80/778/EEC) which set a limit of 0.1 µg/l for individual pesticide compounds. Mecoprop has been detected at low concentrations in drinking water in many countries. A survey of pesticides in groundwater in western Europe (Leistra and Boesten, 1989) found up to 600 mg/l mecoprop in deep groundwater.

According to the Department of the Environment (1994a), mecoprop occurred widely in UK surface waters abstracted for drinking water supply purposes, but few occurrences were reported for groundwater abstracted for this purpose. For the purposes of this present report, data from the Environment Agency's groundwater quality monitoring network for the period 1998-2003 were reviewed. Analysis for mecoprop was undertaken on samples from 980 boreholes and the compound was detected in 105 boreholes (10.7%). Samples from 16 boreholes (1.6%) were found to contain mecoprop at concentrations in excess of 0.1 µg/l, with a maximum reported concentration of 62 µg/l. The boreholes found to contain mecoprop were located in several of the Major Aquifers and were not clustered in any particular geographical region.

2.4 Sources of mecoprop in soil and groundwater

Mecoprop is found in soil/subsoil and groundwater as a result of agricultural or horticultural application as a herbicide, and as a result of disposal of waste herbicide (or herbicide contaminated materials, such as grass cuttings) to landfill, or as tank washings to the ground.

Agricultural and horticultural application of mecoprop is likely to result in diffuse low level influx to the soil and groundwater, with much of the herbicide degrading aerobically in the soil soon after application (Fletcher *et al.*, 1995), or being leached to groundwater or runoff. Concentrations in surface drainage arising from fields subject to normal herbicide application are typically less than 100 µg/l (Fletcher *et al.*, 1995), with concentrations less than 1 µg/l expected in groundwater (de Liphay *et al.*, 2003). Accidental spillage or tank washing during agricultural use may result in short term higher influxes to drainage water or groundwater.

In contrast, disposal of mecoprop to landfill, either directly or on grass cuttings, can result in localised high herbicide loadings to the groundwater. For example, at Helpston UK, around 40 tonnes of mecoprop from tank washings were deposited in landfills during the 1980s. Mecoprop concentrations up to 432,000 µg/l are still observed in the leachate within the landfill (URS, 2002), with up to 3000 µg/l in the groundwater down gradient of the landfills (Williams *et al.*, 2003). Elevated concentrations of mecoprop (up to 600 µg/l at Vejen landfill, Baun *et al.*, 2003; up to 300 µg/l at Sjoelund, Tuxen *et al.*, 2003; up to 975 µg/l at Kolliken, Zipper *et al.*, 1998) have been recorded in groundwater contaminant plumes down-gradient of landfills in Denmark and Switzerland. The authors of this report have experience of a number of existing UK municipal

solid waste (MSW) landfills that were originally constructed as dilute and attenuate landfills, where mecoprop concentrations in groundwater down-hydraulic gradient of the site are up to 100 µg/l. A recent investigation of trace organic components in leachate from over 50 UK landfill sites (MSW and mixed MSW / hazardous wastes) identified mecoprop in 98% of samples, at concentrations up to 140 µg/l (mean = 21.8 µg/l, median = 11 µg/l; Knox *et al.*, 2000).

Long-term usage of a site for maintenance and storage of pesticide application equipment may also result in point source contamination. For example, Reitzel *et al.* (2004) cited an example of one Danish machinery site where groundwater was found to be contaminated with mecoprop at up to 42 µg/l.

3 MECOPROP ATTENUATION PROCESSES

3.1 Dispersion

Mecoprop has a relatively high solubility, so it is readily transported through soils and groundwater by advection. Any plume of a compound moving in water through a porous medium undergoes dispersion ('spreading') and concentrations at a receptor are decreased as a consequence (Domenico and Schwartz, 1998; Environment Agency, 1999). In most hydrogeological systems the amount of dispersion is independent of the solute but in low permeability landfill liners diffusion is the dominant dispersion process and therefore the amount of dispersion is species-dependent (Environment Agency, 2004a).

Broholm (*pers. comm.*, 2003) has found that the diffusion coefficient in free water of mecoprop is approximately $3.9 \times 10^{-10} \text{ m}^2/\text{s}$. This can be included in the dispersion term of solutions to the advection-dispersion equation using the following relationship (Environment Agency, 2004a):

$$D = \alpha v + \frac{D_w}{\tau} \quad (1)$$

where: D is the coefficient of hydrodynamic dispersion (m^2/s),
α is the dispersivity (dispersion length) for the porous medium (m),
v is the advective velocity of groundwater flow (m/s),
 D_w is the diffusion coefficient in free water (m^2/s), and
τ is the tortuosity of the porous medium (dimensionless).

3.2 Sorption

Sorption is the attenuation mechanism by which mecoprop is retained on the surface of a particle (adsorption) or diffuses into a porous material (absorption). Sorption of organic molecules in the subsurface is primarily due to the presence of organic matter in sediments. The degree of sorption of a given organic compound is related mostly to the amount of organic carbon in a sediment, but recently it has become clear that it is also related to the type of organic matter (Allen-King *et al.*, 2002; Steventon-Barnes, 2002; Huang *et al.*, 2003).

Hydrophobic substances (with low water solubility) sorb to aquifer organic matter more readily than hydrophilic (high water solubility) substances. The interaction of organic substances in the environment is related to the octanol-water partition coefficient (K_{ow}), which is defined as the ratio of a chemical's concentration in octanol ($C_{octanol}$) to its concentration in aqueous solution (C_{water}) at equilibrium. For typical groundwater contaminants, K_{ow} varies from roughly 10^{-1} to 10^{10} (Domenico and Schwartz, 1998), with high values indicating strong sorption potential. Therefore, mecoprop, having a K_{ow} of 0.1 will be weakly sorbed.

To quantify the degree of attenuation of mecoprop in the subsurface, the organic carbon-water partition coefficient, K_{oc} and ultimately the soil-water partition coefficient, K_d , must be determined. Empirical estimates for K_{oc} can be derived from simple equations that use the K_{ow} or aqueous solubility; Fetter (1999) presents seventeen such relationships. However, these are strictly for use with non-polar organics, so K_{oc} cannot be derived for mecoprop using these methods. A method for calculating K_{oc} from the molecular architecture of an organic compound is also presented in Fetter (1999) (Box 1). This is general and can be used to determine K_{oc} for polar organics. Assuming that mecoprop can be treated as an organic acid for the purposes of this

analysis, a K_{OC} value of 68 ml/g is obtained. Sorption will be higher for mecoprop applied as an ester due to the hydrophobic properties of the alcohol component of the ester molecule, until the ester is hydrolysed (by biodegradation) to release free acid mecoprop (Felding, 1994).

Box 1. Calculation of K_{OC} values for polar organics using molecular architecture

The first order molecular connectivity index, ${}^1\chi$, is related to the K_{OC} value for polar and non-polar organic compounds. It is calculated by determining the atomic δ value for each non-hydrogen atom in the molecule, which is the number of adjacent non-hydrogen atoms. The connectivity index is then calculated for the molecule with the following formula:

$${}^1\chi = \sum (\delta_i \delta_j)^{-0.5}$$

where δ_i and δ_j are the δ values for a pair of adjacent non-hydrogen atoms and the summation takes place over all the bonds between non-hydrogen atoms of the molecule. Regression analysis has shown that K_{OC} can be calculated using the equation:

$$\log K_{OC} = 0.53 \cdot {}^1\chi + 0.776 - P_f$$

where P_f is an empirical polarity correction factor that accounts for hydrolysis of the molecule. For organic acids, P_f has a value of 2.39.

From Fetter (1999, pp142-143)

The soil-water partition coefficient, K_d , can be obtained from the K_{OC} value with the relationship:

$$K_d = K_{OC} f_{OC} \quad (2)$$

where f_{OC} is the mass fraction of organic carbon in the sediment.

Assuming that the sorption relationship is linear (i.e., the sorbed concentration is directly proportional to the aqueous concentration for the concentration range of interest), K_d can be inserted into any of the standard contaminant transport relationships that utilise the retardation factor approach (e.g. Environment Agency, 1999; Domenico and Schwartz, 1998). Non-linear sorption of organics is dealt with by Allen-King *et al.* (2002), in which a linear absorption model is used to describe diffusion into gel-like organic matter, and a non-linear adsorption model to describe sorption to thermally altered organic material (such as kerogen). This is not discussed further in this report as no mecoprop-specific data exist. Mecoprop in solutions with pH less than the pK_a value (approx. 3.5) will be mostly unionised and will therefore be more likely to sorb to organic materials, so will have a higher K_{OC} . Acetogenic leachate plumes tend not to reach pH values as low as 3.5 but the acidic conditions may have a slight effect on the K_{OC} .

However, in sediments poor in organic matter, the simple linear relationship between K_d and f_{OC} is often not valid and solutes with higher K_{OW} values than mecoprop are preferentially sorbed. Mineral surfaces can then play an important role in retention of organic solutes with low K_{OW} values (Fetter, 1999). Significant sorption to silicate mineral surfaces has been observed for very hydrophobic compounds such as naphthalene (Williamson, 1993). For six non-polar organic compounds, K_d appears to be inversely proportional to the aqueous solubility of a compound (Williamson, 1993) and therefore for a very soluble compound, the K_d may be very low. However,

none of the compounds tested were polar so no conclusions can be made specifically regarding mecoprop.

McCarty *et al.* (1981) present the following relationship for a critical lower fraction of organic carbon (f_{oc}^*) below which sorption to mineral surfaces becomes more important than sorption to organic carbon:

$$f_{oc}^* = \frac{SA}{2 \times 10^5 K_{ow}^{0.84}} \quad (3)$$

where SA is the specific surface area of the sediment (m^2/kg).

Table 3.1 presents estimated values of f_{oc}^* for some typical UK aquifer and aquitard lithologies. With the exception of sand and gravel aquifers, it might be expected that sorption to mineral phases would be more important for attenuation of mecoprop than sorption to organics. In many UK risk assessments it would therefore be conservative to use the f_{oc} model only to predict mecoprop partitioning. This is because, in reality, adsorption to mineral phases or diffusion into smectites would cause greater retardation than the f_{oc} model alone would predict.

Table 3.1 Calculated critical f_{oc}^* values for typical UK lithologies and clay minerals

Lithology / Material	Specific surface area (m^2/kg)	f_{oc}^*	Typical f_{oc} values
Triassic Sherwood Sandstone	1,800 – 8,000 ² 6,000 – 21,000 ⁴	0.007 – 0.086	0.00001 – 0.00071 ¹ 0.0001 – 0.0006 ⁴ 0.0001 – 0.001 ⁵
Sands and gravels	400 – 1,200 ⁴	0.002 – 0.005	0.002 – 0.012 ¹ 0.0002 – 0.0006 ⁴
Glacial Till	10,000 – 50,000 ⁴	0.041 – 0.21	0.00033 – 0.0103 ¹ 0.0017 – 0.0065 ⁴
(pure) kaolinite	6,100 ²	0.025	Very low
(pure) illite	64,000 ²	0.26	Very low
(pure) smectite	138,000 ² 80,000 – 150,000 ³	0.33 – 0.62	Very low

¹ Steventon-Barnes, 2002; ² Haines, 1984; ³ Brady and Weil, 2002; ⁴ Swift, 2003; ⁵ EA & BGS, 2004

It is difficult to predict K_d values for mecoprop when interaction with mineral phases is important. Since mecoprop is an organic acid, the ion will be negatively charged and therefore repelled by negatively-charged clay surfaces at near-neutral pH (Stumm, 1992). In the presence of calcium salts, Clausen *et al.* (2001) observed sorption of mecoprop to kaolinite surfaces and suggested that this was due to the formation of clay-calcium-organic acid complexes. At near-neutral conditions the surfaces of iron oxy-hydroxides are positively charged and organic acids will sorb to the surfaces (Dzombak and Morel, 1990), so K_d may be partly related to the amount of iron oxides in a material. In a typical landfill leachate, there is likely to be considerable competition for the ion exchange sites from other, more plentiful organic acids such as acetic acid, propionic acid and other fatty acids (Department of the Environment, 1995).

Linear sorption models based on K_d values may also be somewhat conservative for sediments with significant organic carbon as sorption can be irreversible in wetland soils (Nilsson *et al.*, 2000). With good site-specific evidence, there might be justification for modification of the advection-dispersion equation to include a decay term (i.e. a pseudo-half life) based on the degree of irreversible sorption (e.g. Fetter, 1999; Baek *et al.*, 2003). However a decay term should not be included without such site-specific data.

3.3 Volatilisation

Volatilisation of organic chemicals from water to the atmosphere is a first-order rate process that occurs near or above the water table and is particularly important for those organics with high vapour pressure and low water solubility (Domenico and Schwartz, 1998). The vapour pressure of mecoprop is extremely low in comparison to other organic compounds and in dilute solutions the loss by volatilisation will be negligible.

3.4 Photochemical degradation

Photochemical degradation (photodegradation) of mecoprop and other phenoxyalkanoic acids has been reported in aqueous solution (see Smith, 1989). Romero *et al.* (1998) identified photodegradation of mecoprop in sterile soils from southern Spain and concluded that, in dry soils, photodegradation at the surface may dominate other transformation pathways, and that photodegradation may be important in the first two days of exposure in moist soils. Smith (1989) observed, however, that since mecoprop is applied to foliage, residues reaching the soil will be partially protected from solar radiation by the crop canopy.

Although it may occur at the ground surface and in surface waters, photodegradation will not be a major mecoprop degradation pathway in soil or groundwater and is not considered further in this report.

3.5 Chemical degradation

Chemical hydrolysis is probably the main mechanism by which mecoprop esters are converted in soil to free acid mecoprop following application of formulations containing the ester (Smith, 1989). However, mecoprop itself is stable to heat, hydrolysis, reduction and atmospheric oxidation (Tomlin, 1997), and there is little evidence for its breakdown in soils in the absence of microbial activity (Smith, 1989).

3.6 Biodegradation

The fundamental principles and kinetics of subsurface biodegradation have been extensively reviewed elsewhere (e.g., Environment Agency, 2002) and will not be described in this report. Few published reports provide information on the most appropriate kinetic models for mecoprop degradation; in this report we have therefore expressed mecoprop biodegradation in terms of 'half-life', i.e. the time taken for contaminant concentration to decrease by 50%, which implies a first-order process.

Mecoprop can be used as a carbon and energy source by microorganisms. This biodegradation can take place under both aerobic and anaerobic conditions, although mecoprop is persistent in many anaerobic samples. As described in the detailed literature review below, a period of acclimation (adaptation) may be required before contaminant biodegradation takes place at a significant rate. This acclimation period may be the result of the time taken for a degradative microbial population to grow to a size that can degrade the contaminant at a clearly measurable rate, or the need for natural genetic and biochemical changes in the microorganisms, or both. Delayed or ineffective degradation of mecoprop may be a polyauxic effect, i.e., the microbial population will preferentially degrade other (easier or energetically beneficial) substances in preference to mecoprop.

The metabolic pathway involved in the degradation of mecoprop has been elucidated (Figure 2). 4-chloro-2-methylphenol (4-CMP; also known as chlorocresol or PCOC) has been identified as the primary initial transformation product in laboratory culture (Nickel *et al.*, 1997; Tett *et al.*,

1994), soils (Smith, 1989; Clint *et al.*, 1993) and groundwater (Harrison *et al.*, 2003). Further degradation then occurs by hydroxylation at the 6-position of the 4-CMP, followed by cleavage of the aromatic ring.

4-CMP is highly toxic to aquatic organisms (Harrison *et al.*, 2003), and has been determined as a List I substance for the Groundwater Regulations (JAGDAG, 2001), but the majority of studies suggest that further transformation of 4-CMP is a rapid process. For example, Broholm *et al.* (2001) reported no accumulation of substituted phenols or other intermediates during aerobic mecoprop degradation. Nitschke *et al.* (1999) studied the toxicity to aquatic organisms of mecoprop degradation products following aerobic degradation in a sewage sludge treatment system, and demonstrated that these were not significantly toxic to aquatic life. However, Harrison *et al.* (2003) observed that, under anaerobic conditions, degradation of 4-CMP did not appear to occur until all of the mecoprop had been utilised.

Reitzel *et al.* (2004) undertook a literature review of production history and degradation pathways for phenoxy herbicides and reported that the metabolites of the herbicides (particularly 4-CMP) are also frequent impurities in the herbicide products, with impurities potentially making up more than 30% of the herbicide product. 4-CMP is also an impurity within, and degradation product of, the related herbicide MCPA ((4-chloro-2-methylphenoxy)acetic acid). This makes it difficult to relate the presence of 4-CMP in environmental samples to mecoprop biodegradation.

A number of studies have suggested that the R- and S-isomers of mecoprop may degrade at different rates (e.g. Buser and Muller, 1998; Romero *et al.*, 2000; Zipper *et al.*, 1996) but there is no consistency in which of the isomers is the more rapidly degraded. Where differential rates of degradation have been observed, the relative proportion of the R- and S-isomers has been used to study degradation pathways (e.g. Environment Agency, 2001b; Muller and Buser, 1997; Kohler *et al.*, 1999; Williams *et al.*, 2003). The enantiomeric fraction (EF) has been employed to report the relative proportions of the isomers in samples and is defined as:

$$EF = [R] / [R] + [S] \quad (4)$$

EF can range from 0 (completely S-isomer) to 1 (completely R-isomer), with a racemic mixture having an EF = 0.5. An increase in EF therefore represents a relative decrease in the proportion of S-isomer within a mixture. However, enantiomeric fractions may also be altered by enzyme-catalysed chiral inversion (Williams *et al.*, 2001) and EF may therefore be of limited value as an indicator of enantiomer-specific biodegradation.

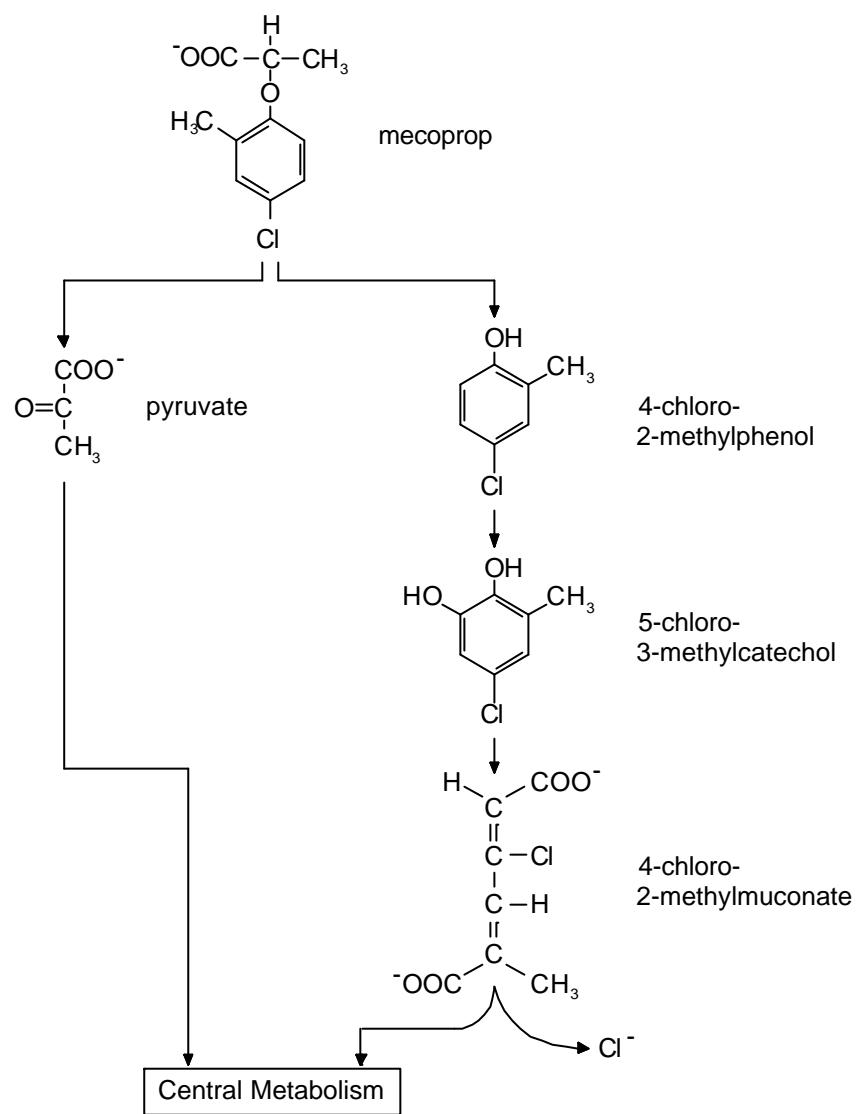


Figure 2. Biodegradation pathway for mecoprop. Putative metabolic pathway based on Nickel et al. (1997), Smith (1989) and Tett et al. (1994).

4 LITERATURE REVIEW - TOPSOIL

4.1 Introduction

The fate and behaviour of phenoxy herbicides (which include mecoprop) in soil have been studied quite extensively, particularly for agricultural and pesticide research (reviewed by Smith, 1989). The literature specifically on mecoprop is smaller and has been reviewed in the Department of the Environment Pesticide Evaluation reports for Mecoprop and Mecoprop-P (Department of the Environment, 1994a, b). More recently the environmental fate of mecoprop in soils has been studied in conjunction with aquifer degradation studies (e.g., Larsen *et al.*, 2000; Johnson *et al.*, 2000; Albrechtsen *et al.*, 2001).

4.2 Sorption

As described in Section 3.2 sorption of mecoprop to soils is likely to be low because of the high polarity and negative charge of the mecoprop molecule in neutral conditions. Mecoprop sorption is primarily related to the humus content of the soil (Smith, 1989; Fomsgaard, 1997) but Smith (1989) suggests that adsorption of phenoxy acids to organic matter is unlikely to seriously affect biodegradation, since laboratory experiments showed similar biodegradation rates in soils containing between 4% and 12% organic matter.

Kristensen *et al.* (2001) observed no adsorption of mecoprop in Danish soil samples with an organic content of 1.3%. By contrast Nilssen *et al.* (2000) describing the results of experiments studying the fate of mecoprop and isoproturon in groundwater discharging to a freshwater wetland site in Denmark, found that mecoprop was attenuated by 25 to 75% compared to the conservative bromide tracer employed. However they found no evidence for degradation within the residence time of the tests. Batch experiments indicated that 90-95% of the added pesticide was irreversibly adsorbed after a few hours to a few days but the paper did not provide specific sorption data.

Literature K_d and K_{OC} values for mecoprop in soils are summarised in Table 4.1.

Table 4.1 Literature K_d and K_{OC} values for mecoprop in soils.

Reference	K_d (ml/g)	K_{OC} (ml/g) ¹	foc of soil used for K_{OC} determination
Kristensen <i>et al.</i> , 2001	0	0	0.013
Harris <i>et al.</i> , 2000	0.61	(18.5)	0.033
Helweg, 1993	0.07 – 0.2	5.3 – 13.3	0.024 – 0.026
Department of the Environment 1994a, b	-	11 – 25	-
Fomsgaard, 1997	0.0 – 0.07	(0 – 7)	0.002 – 0.01
Fomsgaard, 1997	0.4 – 0.8	(20)	0.02 – 0.04
Fomsgaard, 1997	2.6 – 2.8	(50.9 – 59.6)	0.047 – 0.051

¹ Values in brackets have been calculated for this report.

4.3 Biodegradation

4.3.1 Reported mecoprop half-lives

Mecoprop half-lives reported from laboratory and field experiments with topsoil by a wide range of authors are shown graphically in Figure 3 and summarised in Table 4.2.

In topsoil, the half-life of mecoprop appears to be typically less than 15 days, although longer half-lives have been recorded in some conditions, as discussed below. Mecoprop has not been found to degrade in topsoil under anaerobic conditions.

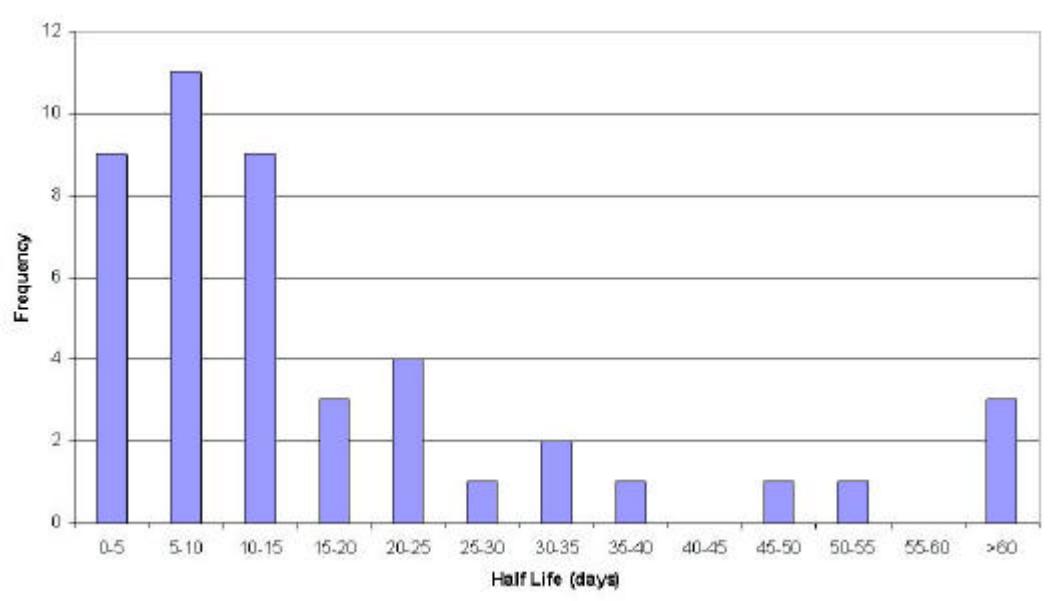


Figure 3. Distribution of identified literature values of half-lives for mecoprop in topsoil.

Table 4.2 Literature half-lives for mecoprop under different conditions in topsoil

Author	Soil Type	Enantiomers	Conditions	Half-life (days)
Department of the Environment (1994a)	Sandy loam	Mixed	Aerobic, 25°C	13.3
Department of the Environment (1994a)	Sandy loam	Mixed	Anaerobic, 25°C	No degradation
Brooke and Matthiessen (2001)	Not specified	Mixed	Aerobic, field temperature	3.3
Harris <i>et al.</i> (1994)	Clay	Mixed	Aerobic	4.5
Helweg (1993)	Sandy loam	Mixed	Aerobic, 20°C, 2 mg/kg	3
Helweg (1993)	Sandy loam	Mixed	Aerobic, 10°C, 2 mg/kg	12
Helweg (1993)	Sandy loam	Mixed	Aerobic, 5°C, 2 mg/kg	20
Helweg (1993)	Sandy loam	Mixed	Aerobic, 20°C, 2 mg/kg	10
Helweg (1993)	Sandy loam	Mixed	Aerobic, 20°C, 2 mg/kg	15
Helweg (1993)	Sandy loam	Mixed	Aerobic, 20°C, 0.2 mg/kg	1.3
Helweg (1993)	Sandy loam	Mixed	Aerobic, 20°C, 2 mg/kg	3
Helweg (1993)	Coarse sand	Mixed	Aerobic, 20°C, 2 mg/kg	4
Johnson <i>et al.</i> (2000)	Chalky topsoil	Mixed	Aerobic, 20°C, 100 µg/l	62
Johnson <i>et al.</i> (2003)	Sandstone topsoil	Mixed	Aerobic, 20 °C, 100 µg/l	69
Johnson <i>et al.</i> (2003)	Limestone topsoil	Mixed	Aerobic, 20 °C, 100 µg/l	<102
Kirkland <i>et al.</i> (1972) in Smith (1989)	Sandy loam	Mixed	Aerobic, 23 °C, 3 mg/kg	10
Larsen <i>et al.</i> (2000)	Sandy	Mixed	Aerobic, 10°C, 2.2 µg/kg	19
Larsen <i>et al.</i> (2000)	Sandy	Mixed	Aerobic, 10°C, 2.2 µg/kg	28
Lindholm <i>et al.</i> (1982) in Department of the Environment (1994a)	Finnish soil	Mixed	Aerobic, 22 °C, 5 - 15 mg/kg	20
Lindholm <i>et al.</i> (1982) in Smith (1989)	Clay	Mixed	Aerobic, 22 °C, 5mg/kg	3
Lindholm <i>et al.</i> (1982) in Smith (1989)	Clay	Mixed	Aerobic, 22 °C, 15mg/kg	3
Romero <i>et al.</i> (2000)	Silt loam	Mixed	Aerobic, 15 °C, 1 mg/kg dry soil	15
Romero <i>et al.</i> (2000)	Silt loam	R-	Aerobic, 15 °C, 1 mg/kg dry soil	12
Romero <i>et al.</i> (2000)	Silt loam	S-	Aerobic, 15 °C, 1 mg/kg dry soil	21
Romero <i>et al.</i> (2000)	Sandy loam	Mixed	Aerobic, 15 °C, 1 mg/kg dry soil	11
Romero <i>et al.</i> (2000)	Sandy loam	R-	Aerobic, 15 °C, 1 mg/kg dry soil	8
Romero <i>et al.</i> (2000)	Sandy loam	S-	Aerobic, 15 °C, 1 mg/kg dry soil	12
Romero <i>et al.</i> (2000)	Clay loam	Mixed	Aerobic, 15 °C, 1 mg/kg dry soil	50
Romero <i>et al.</i> (2000)	Clay loam	R-	Aerobic, 15 °C, 1 mg/kg dry soil	77
Romero <i>et al.</i> (2000)	Clay loam	S-	Aerobic, 15 °C, 1 mg/kg dry soil	32
Romero <i>et al.</i> (2000)	Silt loam	R-	Aerobic, 15 °C, 1 mg/kg dry soil	4
Romero <i>et al.</i> (2000)	Sandy loam	R-	Aerobic, 15 °C, 1 mg/kg dry soil	7
Romero <i>et al.</i> (2000)	Clay loam	R-	Aerobic, 15 °C, 1 mg/kg dry soil	40
Romero <i>et al.</i> (2000)	Peat amended silt loam	Mixed	Aerobic, 15 °C, 1 mg/kg dry soil	14
Romero <i>et al.</i> (2000)	Peat amended silt loam	R-	Aerobic, 15°C, 1 mg/kg dry soil	10
Romero <i>et al.</i> (2000)	Peat amended silt loam	S-	Aerobic, 15 °C , 1 mg/kg dry soil	21
Romero <i>et al.</i> (2000)	Peat amended sandy loam	Mixed	Aerobic, 15 °C, 1 mg/kg dry soil	14
Romero <i>et al.</i> (2000)	Peat amended sandy loam	R-	Aerobic, 15 °C, 1 mg/kg dry soil	10
Romero <i>et al.</i> (2000)	Peat amended sandy loam	S-	Aerobic, 15 °C, 1 mg/kg dry soil	22
Romero <i>et al.</i> (2000)	Peat amended clay loam	Mixed	Aerobic, 15 °C, 1 mg/kg dry soil	33
Romero <i>et al.</i> (2000)	Peat amended clay loam	R-	Aerobic, 15 °C, 1 mg/kg dry soil	21
Romero <i>et al.</i> (2000)	Peat amended clay loam	S-	Aerobic, 15 °C, 1 mg/kg dry soil	53
Smith and Aubin (1991) in Department of the Environment 1994a	Unexposed/ pre-exposed soils	Mixed	Aerobic, 15 °C, 1 mg/kg dry soil	10
Smith and Hayden (1981) in Department of the Environment 1994a	Clay loam	Mixed	Aerobic, 20 °C, 2 mg/kg	9
Smith and Hayden (1981) in Department of the Environment 1994a	Sandy loam	Mixed	Aerobic, 20 °C, 2 mg/kg	7
Smith and Hayden (1981) in Smith (1989)	Clay	Mixed	Aerobic, 20 °C, 2 mg/kg	8
Smith and Hayden (1981) in Smith (1989)	Clay loam	Mixed	Aerobic, 20 °C, 2 mg/kg	9
Smith and Hayden (1981) in Smith (1989)	Sandy loam	Mixed	Aerobic, 20 °C, 2 mg/kg	7
Minimum				1.3
Maximum				102
Median				12
Mean				20

Apart from Brooke and Matthiessen (1991), there are relatively few UK studies, and the majority of the data presented in Table 4.2 are for Spain or Canada where climate and soil are substantially different to the UK. Helweg (1993), studied soil and subsoil at three different locations in Denmark, and found mecoprop half-lives between 1.3 and 20 days depending on conditions. Larsen *et al.* (2000), also working in Denmark, observed rapid degradation rates in the top 300mm 'ploughed layer' of a sandy soil, where they obtained a half-life of around 20 days. Romero *et al.* (2000) looked at enantiomeric effects on degradation rates in various calcareous soils from Spain and recorded half-lives of between 8 and 77 days.

In their comparison of mecoprop degradation in UK soils and underlying aquifers, Johnson *et al.* (2003) reported that mecoprop added to soils at 100 µg/l degraded under aerobic conditions in all of the soil samples tested. Half-lives were between 62 and 100 days. The degradation rates recorded were generally lower than those reported elsewhere but the authors noted that there was no history of herbicide use at the subject sites and that these half-lives may therefore have been longer than would have been the case for acclimated soils.

Department of the Environment (1994a) collated data from a number of US, Canadian and European studies and concluded that mecoprop degrades rapidly in soil under aerobic laboratory conditions and half-lives generally ranged from 7 to 19 days at 20°C. It was concluded that the rate of degradation was little affected by the application rate, by acclimation or by treatment with a range of other pesticides. However, other studies have demonstrated that various factors do appear to affect the degradation rate, as described below.

4.3.2 Effect of concentration

In a more general study of phenoxy acid herbicides, Smith (1989) concluded that there was some evidence for concentration affecting their degradation in soils. Breakdown according to first order kinetics (with no lag period) was observed in soil concentrations below about 10 mg/kg, while at higher concentrations (up to *circa* 500 mg/kg) an increased rate of degradation was reported following a lag period. The lag period was interpreted as the time taken for acclimation (adaptation) of the microbial communities to pesticide biodegradation.

In contrast, Helweg (1993) found faster initial degradation of mecoprop and a shorter half-life at 0.2 mg/kg compared to 2 mg/kg.

4.3.3 Pre-exposure of soil to mecoprop

If mecoprop has previously been used on the site, then more rapid degradation is likely to occur (Roeth, 1984; Smith, 1989). This is consistent with acclimation being required to develop an active degradative microbial community.

4.3.4 Effect of temperature

Soil temperature may also have an effect on mecoprop degradation, with slower degradation below 10°C (Smith, 1989). Helweg (1993) found longer half-lives at 5°C compared to 20°C but little attempt has been made to quantify the relationship between temperature and mecoprop biodegradation rate.

4.3.5 Effect of moisture content

As with all microbial processes, Smith (1989) noted that soil moisture is likely to affect mecoprop degradation rates in soils. This was confirmed by Helweg (1993) who found longer half-lives in dry soil and in flooded soil compared to moist soil.

4.3.6 Effect of depth

Helweg (1993) found considerable variability in degradation rates in soil samples collected from 33 – 99cm below surface, but slower degradation than within the topsoil. Larsen *et al.* (2000) reported similar results with rapid degradation (half-life c. 20 days) in the top 300mm, but steadily increasing to >5 years at depths over 4.5 m bgl. The effect of depth is discussed further for subsoils in Section 5.

4.3.7 Effect of redox conditions

Very few studies of mecoprop degradation in anaerobic surface soil have been published and Department of the Environment (1994a) reported that mecoprop does not degrade under anaerobic conditions. Nilsson *et al.* (2000) studied the fate of mecoprop in a freshwater wetland, with laboratory studies and a field injection experiment with groundwater discharging to anaerobic wetlands. They recorded little degradation within the residence time of 20-40 days in laboratory experiments under sulphate-reducing conditions.

4.3.8 Effect of pH

Smith (1989) reviewed evidence for pH influence on phenoxyalkanoic degradation rates in soils. No mecoprop specific data was identified. Results from experiments with other herbicides suggested that although soil pH may influence degradation rates of phenoxyalkanoic acids, no general conclusions could be drawn as to the effects of soil pH on persistence because of the possibility of wide variation in soil microflora in the experimental set-up. Fomsgaard and Kristensen (1999) observed no influence of pH on adsorption or degradation in topsoils with pH in the range 5.5 – 6.9.

Biological activity is generally greatest in the pH 6-8 range and there is likely to be little mecoprop degradation at pH <5 or pH >9 (Brady and Weil, 2002).

4.3.9 Effect of application method and timing

According to Gustafson (1989; cited by Felding, 1994) the risk of leaching is greatest for pesticides that are applied in the autumn because extra precipitation increases leaching and lower winter temperatures reduce degradation. This was observed by Brooke and Matthiessen (2001) when a November rain storm caused leaching of mecoprop into a stream (up to 11 µg/l) adjacent to their application area.

Felding (1994) studied the leaching of phenoxy acids from farmland to subsoil by collecting samples of water from below the root zone in locations with different treatment histories. Mecoprop was found to be present in the sub soil several months after application, and it was suggested that application timing and formulation were major factors controlling the leaching of mecoprop to the subsurface. The study showed that spraying with mecoprop salts in the spring at one site resulted in leaching of the acid to the subsoil, whereas spraying with the ester in the autumn at another site did not result in leaching of the mecoprop acid released by hydrolysis. It was concluded that the ester formulation was probably adsorbed to the soil and subsequently slowly desorbed, whereas the adsorption of the salt was significantly less.

4.3.10 Enantiomeric effects

Tett *et al.* (1994) studied bacterial degradation of mecoprop in topsoil in aerobic laboratory cultures. They found that only the R-isomer was degraded, and that degradation rates increased after prolonged incubation.

Romero *et al.* (2000) compared degradation of racemic mecoprop and pure isomers (R-isomer and S-isomer) in different calcareous and peat-amended soils from Spain (Table 4.2). They recorded half-lives of between 8 and 77 days, with the fastest degradation in sandy loam, and the slowest degradation in unamended clay soil. The R-isomer degraded faster in the sandy loam and silty loam and in the peat-amended clay. The S-isomer degraded faster in the unamended clay soil.

4.4 Effect of climatic conditions on mecoprop fate

A number of studies have shown that climatic conditions, in particular timing of rainfall following application, can have a major effect on mecoprop fate and transport following surface application. Since mecoprop is mobile and poorly adsorbed, it is vulnerable to leaching if there is rainfall in the period after application and before degradation. As described above, Gustafson (1989) concluded that (at least in Denmark) the risk of leaching is greatest for pesticides that are applied in the autumn because extra precipitation increases leaching and lower winter temperatures reduce degradation. This is also likely to be applicable to the UK.

Harris *et al.* (1994) and Harris *et al.* (2000) reported on detailed studies of pesticide leaching in UK cracking clay soils, using 0.2 hectare plot lysimeters. They reported a mecoprop half-life of 4.5 days in the topsoil. In the leaching study, reported in detail, there was little rainfall in the period following application and no mecoprop was detected in the drainage waters from the plot, implying degradation was complete before drainage occurred.

In contrast, Fletcher *et al.* (1995) studied mecoprop discharge from agricultural land to a salt marsh system in Essex. Immediately following mecoprop application in late spring a slight increase in mecoprop concentration was observed in the drainage ditches. Heavy rainfall occurred 10 days after mecoprop application, resulting in an increase to a peak value of 25.8 µg/l mecoprop in the drainage ditches. Within 7 days of the major rainfall event the mecoprop concentration had decreased to only 20% of the peak value, and 35 days after application concentrations were below detection limits despite further heavy rain, implying that no further mecoprop was available for leaching.

5 LITERATURE REVIEW – UNSATURATED SUBSURFACE FORMATIONS

5.1 Introduction

In contrast with topsoil and groundwater, very few studies of mecoprop behaviour in the unsaturated zone have been identified in the literature review. Those studies that have been identified comprise comparisons between degradation rates in topsoil, aquifer and subsoil or unsaturated subsurface rock.

5.2 Sorption

No specific studies of mecoprop sorption in subsoils have been identified in this literature review. The processes controlling mecoprop sorption in subsoils will be similar to those in topsoil (Section 4) and aquifers (Section 6). It is likely, however, that f_{OC} values of the subsoil (unsaturated zone largely comprising weathered bedrock) will be significantly less than that of the overlying topsoil. Accordingly, the potential for sorption is expected to be significantly lower than in the relatively organic-rich topsoil.

5.3 Biodegradation

A number of laboratory experiments have included studies of the mecoprop degradation potential of samples from subsoil or the unsaturated zone.

Studies comparing degradation rates vertically from topsoil have demonstrated a reduction in degradation rate with depth. Helweg (1993) observed an increase in half-life from 7 days at 0-33 cm bgl to between 34 and 70 days in samples collected from between 33 cm and 1 m bgl.

Albrechtsen *et al.* (2001) and Larsen *et al.* (2000) undertook laboratory batch studies to compare degradation rates at various subsoil depths in sandy sediments from Denmark. They measured a decrease in mecoprop degradation rate with depth, from a half-life of 19 days at 0.06 m bgl to 1 to 7 years at 3.4 m bgl. Albrechtsen *et al.* (2003) reported degradation in aerobic laboratory batch studies using samples from limestone from the unsaturated zone at Breville in France. Specific degradation rates were not presented but the rate of degradation was described as decreasing with depth.

Johnson *et al.* (2000) compared the mecoprop degradation potential of topsoil, unsaturated zone and aquifer samples from the Chalk in Hampshire. They showed mecoprop degradation in the topsoil but no degradation over 200 days in unsaturated zone Chalk. Similarly, in a wider study including the Triassic Sherwood Sandstone and Lincolnshire Limestone, Johnson *et al.* (2003) found degradation in topsoil but not in samples from the unsaturated subsoil.

6 LITERATURE REVIEW - GROUNDWATER

6.1 Introduction

The literature on the fate of mecoprop in groundwater is not large, and appears to be restricted to a small number of research teams, most notably researchers at the Danish Technical University. The Danish research has included laboratory and field studies of point source contamination such as landfills and machine storage sites, artificial field injection studies, and laboratory and in-situ microbiological experiments at a range of pesticide concentrations and focused on naturally aerobic sandy Quaternary and Cretaceous Chalk aquifers. Some laboratory studies of mecoprop degradation potential of aquifer sediments and waters from elsewhere in mainland Europe have also been undertaken.

In the UK, research on the fate of mecoprop in aquifers has focussed on Helpston, where groundwater in the Lincolnshire Limestone is heavily contaminated with mecoprop from former landfills. Other UK studies have been performed at field sites located on the Chalk, Triassic Sherwood Sandstone and Lincolnshire Limestone.

The literature search has not revealed any published research into mecoprop degradation in groundwater in the United States or Canada, with the exception of one Danish co-authored paper (Agertved *et al.*, 1992) reporting on a mecoprop field injection trial at the Borden site in Ontario, Canada.

6.2 Sorption

Adsorption of mecoprop to most aquifer materials (particularly clay minerals and organic matter) is expected to be low because of the high polarity and negative charge of the mecoprop molecule in neutral conditions. Sorption to iron oxide coated aquifer materials, such as is common in the Triassic Sandstone aquifer, may be more important since these oxide minerals retain a net-positive charge over the pH range found in most aquifers. Sorption may be expected to increase at lower pH as it will affect both the surface charge of the rock forming minerals, and the degree of dissociation of the carboxylic acid group (Madsen *et al.*, 2000).

Several authors have reported on laboratory experiments regarding the adsorption of mecoprop to specific substrates. Clausen *et al.* (2001) studied the adsorption of pesticides onto quartz, calcite, kaolinite and α -alumina. They found adsorption of anionic pesticides (including mecoprop) could only be measured when positively charged sites were present on the mineral surface, and that adsorption of mecoprop onto kaolinite was detectable in the presence of CaCl_2 electrolyte. Madsen *et al.* (2000) investigated mecoprop adsorption onto Danish aquifer sediments and found that, as expected, sorption of mecoprop depended largely on pH, being higher at low pH (<6.7) compared to high pH (>7.4). They found that the sorption capacity for chalk aquifers was higher than for sandy aquifers at pH 6. Zipper *et al.* (1998) found very low adsorption to sandstone and marl and higher adsorption on to amorphous silica (SiO_2) and montmorillonite. Environment Agency (2004b) report no significant sorption of mecoprop to a siltstone with relatively high organic carbon content ($f_{\text{OC}} = 0.0105$) for aquifer material. They recorded more adsorption at lower concentrations. Zipper *et al.* (1998) could detect no significant difference in adsorption between the R- and S-isomers of mecoprop.

Retardation by adsorption of mecoprop in natural systems has been investigated by a number of authors by comparison of mecoprop retardation with tracers such as bromide or chloride. No significant mecoprop retardation was observed in the continuous field injection studies in the

sandy aquifers at Vejen (Broholm *et al.*, 2001) or Borden, Ontario (Agertved *et al.*, 1992), or in the anaerobic landfill plume in the sandy aquifer at Grindsted (Rugge *et al.*, 1999).

Distribution coefficients calculated from laboratory experiments on aquifer sediments are summarised in Table 6.1.

Table 6.1 Literature sorption values for mecoprop in aquifers

Author	K _d (ml/g)	f _{oc}	K _{oc} ¹	Lithology
Zipper <i>et al.</i> , 1998	< 1	n/a	n/a	Sandstone and marl
Tuxen <i>et al.</i> , 2000	0 – 0.04	0.0002	(0 – 200)	Sand and gravel
Pedersen, <i>pers. comm.</i>	Average 0.4	n/a	n/a	Sand
Madsen <i>et al.</i> , 2000	0.07 – 0.26	0.0002 – 0.0005	(140 – 1,300)	Sand
Madsen <i>et al.</i> , 2000	0.17	0.00003 – 0.0012	(140 – 5,700)	Chalk
Env. Agency, 2004b	0.003 – 0.11	0.0105	(0.29 – 10.5)	Siltstone

¹ Values in brackets have been calculated for this report.

6.3 Biodegradation

Biodegradation of mecoprop in aquifers has been studied in the laboratory, in field studies at mecoprop contaminated sites (particularly landfills) and in field injection experiments.

6.3.1 Biodegradation in aerobic aquifers

Many, but not all, studies of the mecoprop degradation potential in aquifer sediments have demonstrated aerobic degradation.

The Vejen site, Denmark

Heron and Christensen (1992) demonstrated aerobic degradation of mecoprop at 65 – 1400 µg/l in laboratory batch studies of sandy sediments collected from an unpolluted aquifer at Vejen, Denmark. Following a lag period of 20 to 110 days, they observed stepwise degradation of half of the mecoprop, followed by the remaining mecoprop after another lag period. This stepwise degradation was interpreted as the result of enantiomeric effects. They observed mineralisation over 200 days at all concentrations studied but noted variable degradation rates in samples collected only a few metres apart.

Also at Vejen, field injection trials of pesticides in an otherwise unpolluted sandy aquifer were undertaken (Broholm *et al.*, 2001; Rugge *et al.*, 2002). Mecoprop was injected over a seven month period from November 1998, with concentrations around 40 µg/l measured immediately down-gradient of the injection wells. The trials demonstrated rapid aerobic degradation of the mecoprop following an initial lag (adaptation) period of 80 – 120 days (Broholm *et al.*, 2001). No differential degradation of R or S-isomers was observed (Rugge *et al.*, 2002).

Subsequently, a number of studies were made to assess the effect of exposure on biodegradation. In laboratory studies, Torang *et al.* (2003) found rapid degradation with no lag time at mecoprop concentrations of 100 µg/l in samples collected from the aquifer that had been previously heavily exposed to mecoprop during the field injection studies. At the same mecoprop concentration they found rapid degradation following a lag time of 35 days in lightly exposed aquifer, but no degradation over 100 days at any concentration in previously unpolluted aquifer samples. Torang *et al.* (2003) also studied the effect of very low mecoprop concentrations, and found that concentrations below 10 µg/l, although degraded, did not show any increase in degradation rate with time, implying that there was insufficient mecoprop concentration to permit development of a large degradative microbial community.

Other Danish sites

Studies at other sites have reported variable mecoprop degradation potential in groundwater and aquifer samples.

Albrechtsen *et al.* (2001) found no mecoprop degradation over 371 days at 50 µg/l in laboratory batch studies on samples from 8 aerobic and anaerobic Danish aquifers. Similarly, Pedersen (pers. comm.) found no mecoprop degradation at similar concentrations over a similar period in any of the Danish aquifer samples studied (including samples from aerobic, denitrifying, manganese and iron-reducing, sulphate-reducing and methanogenic environments). In contrast, Albrechsten *et al.* (2003) demonstrated mecoprop degradation in 7 out of 8 European aerobic aquifers studied but detected no degradation in 2 anaerobic aquifers.

UK aerobic aquifers

Johnson *et al.* (2000), undertook laboratory studies comparing the mecoprop degradation potential of surface soils and the underlying aquifer in the Hampshire Chalk. They found mecoprop degradation in the soil, but could not identify any degradation over 200 days in samples from the underlying unpolluted Chalk aquifer, spiked with mecoprop at 100 µg/l. In similar studies at other UK locations, Johnson *et al.* (2003), observed mecoprop degradation in groundwater from some (but not all) boreholes in the Triassic Sherwood Sandstone aquifer but from none of the samples from unpolluted Lincolnshire Limestone or Chalk.

6.3.2 Biodegradation in anaerobic aquifers

As described above, Albrechtsen *et al.* (2001, 2003) and Pedersen (pers. comm.) found no mecoprop degradation in anaerobic aquifer samples from Denmark and elsewhere in mainland Europe.

Larsen and Aamand (2001) undertook laboratory batch studies assessing the mecoprop degradation potential of anaerobic Danish aquifer samples. They found 3% reduction in mecoprop concentrations after 312 days in separate anaerobic denitrifying and methanogenic aquifers, but no reduction in concentration in samples from an anaerobic sulphate-reducing aquifer.

Biodegradation in landfill leachate plumes

The lack of degradation of mecoprop under anaerobic conditions means that where it has been disposed to landfill it is frequently among the most persistent organic compounds in the landfill plume, since most landfill plumes are anaerobic (Department of the Environment, 1995). Mecoprop concentrations in landfill leachate plumes are also typically much higher than those arising from normal pesticide applications (Knox *et al.*, 2000).

A number of studies have also been undertaken on the behaviour of mecoprop in the plume environment.

Helpston, UK

In the UK, mecoprop fate and transport in groundwater has been extensively studied at the Helpston landfills located in the Lincolnshire Limestone north-west of Peterborough (Harrison *et al.*, 1998 and 2003; Williams *et al.*, 2001 and 2003; Environment Agency, 2001b). Approximately 40 tonnes of mecoprop from tank washings was disposed to landfill in the 1980s. In 1987 groundwater abstracted from a public water supply borehole 2.5 km downgradient from the landfill started to show increasing concentrations of mecoprop, increasing to 8 µg/l by 1992.

Harrison *et al.* (1998) used borehole and laboratory microcosms to investigate the effect of redox conditions on mecoprop degradation, comparing a borehole located in an iron-reducing portion of the plume with an aerobic borehole further away from the landfill. They found no degradation in

the anaerobic microcosms, and rapid degradation in the aerobic microcosms, with a short lag period (4 days) followed by degradation to below detection limits after 10 days.

Williams *et al.* (2001) studied enantiomeric ratios of the mecoprop in the groundwater at Helpston and tried to use the data to understand natural attenuation processes at the site. Under the sulphate-reducing conditions that predominated in fresh leachate and close to the landfill, R- and S-isomers were present as a racemic mixture, and no mecoprop degradation is observed to take place. Further down-hydraulic gradient from the landfill, the redox conditions were iron, manganese and nitrate-reducing and large decreases in the mecoprop enantiomeric fraction are observed. These were originally interpreted as indicating inversion of R-mecoprop to S-mecoprop (Williams *et al.*, 2001) but subsequently re-interpreted (Williams *et al.*, 2003) as indicating preferential degradation of the R-isomer, based on laboratory results (Harrison *et al.*, 2003; see below). In the distal part of the plume, redox conditions were generally manganese and nitrate-reducing and there was a large increase in the enantiomeric fraction, interpreted as faster degradation of the S-isomer. Locally where the distal plume encounters sulphate-rich connate water, conditions are sulphate-reducing and mecoprop again persists.

Harrison *et al.* (2003) described the results of further microcosm experiments using samples from boreholes located in a wider range of redox conditions in the Helpston landfill plume. No degradation was observed in anaerobic microcosms from the methanogenic or sulphate-reducing zones. However, microcosms set up with groundwater samples from the same boreholes but under aerobic conditions showed aerobic degradation after lag periods of between 20 and 100 days, with the S-isomer degrading slightly faster than the R-isomer.

Microcosms set up with samples from boreholes in the nitrate-reducing zone showed degradation of the R-isomer only, as observed in the field studies by Williams *et al.* (2001). No degradation was initially observed in samples from iron-reducing conditions, but after addition of nitrate to induce nitrate-reducing conditions, degradation was observed after a lag period of 21 days. Microcosms from nitrate-reducing or aerobic zones, which had exhibited enantioselective biodegradation of the R-isomer when kept under anaerobic conditions, showed rapid biodegradation of both isomers (6 days) with no lag time under aerobic conditions.

Harrison *et al.* (2003) found no evidence of enantiomeric inversion in any of the microcosms.

Kollikon, Switzerland

Zipper *et al.* (1998) studied mecoprop distribution in leachate and groundwater associated with an old landfill at Kollikon in Switzerland. The landfill, located in fractured marls and calcareous sandstone, received chemical waste including pesticides from 1979 to 1985. The aquifer is naturally aerobic to nitrate-reducing, but locally in the area of the landfill plume sulphate-reducing to methanogenic conditions are found. Mecoprop was found within the leachate at concentrations up to 124 µg/l, in a racemic mixture (equal proportions of R- and S-isomers). Mecoprop concentrations in the aquifer ranged from <0.001 to 975 µg/l, with an up to 7-fold excess in the R-isomer, interpreted as indicating preferential degradation of the S-isomer. Degradation rates could not be calculated from the data collected and the variation in concentration in the aquifer was interpreted as related to varying source supply concentrations and rates.

Vejen, Denmark

Mecoprop degradation within a landfill plume has also been studied in the sandy aquifer at Vejen in Denmark. According to Baun *et al.*, 2003, this naturally aerobic aquifer is locally anaerobic down-gradient of the landfill, with methanogenic conditions 0-40 m from the landfill and iron-reducing conditions predominant beyond. Lyngkilde and Christensen (1992) noted the persistence of mecoprop in the landfill plume, observing that, of all the xenobiotic contaminants observed in the leachate, only mecoprop was detected 100 m down-gradient. Baun *et al.* (2003) observed no evidence of mecoprop degradation in the aquifer, and concluded that

dilution/dispersion alone could account for the decrease in mecoprop concentration from 600 µg/l at the border of the landfill to 26 µg/l at a distance 135 m down-gradient.

Grindsted, Denmark

Mecoprop degradation within the anaerobic environment of a landfill plume has also been studied at the Grindsted landfill in Denmark (Rugge *et al.*, 1999). Degradation studies included field injection studies, in-situ microcosms and laboratory batch studies, including locations within the methanogenic zone and iron-reducing zones. Mecoprop was added to each of the experiments at concentrations around 150 µg/l. No degradation was observed in any of the experiments.

Sjølund, Denmark

Tuxen *et al.* (2003) reported that there is significant mecoprop attenuation in the nitrate and iron-reducing anaerobic landfill plume that cannot be explained by dilution or sorption. Laboratory experiments demonstrated mecoprop degradation in anaerobic microcosms using samples from the anaerobic zone. In the distal plume, aerobic degradation was interpreted as the major process resulting in mass loss.

6.3.3 Enantioselectivity of degradation processes in groundwater

Williams *et al.* (2001, 2003) have proposed that mecoprop enantiomeric fractions can be used as evidence for natural attenuation of mecoprop but fractionation has been relatively little studied in groundwater (but more widely studied in the topsoil and surface waters e.g. Muller and Buser, 1997; Buser and Muller 1998; Kohler *et al.*, 1999).

As discussed above, some aquifer studies have suggested enantioselective degradation of mecoprop in groundwater but this has been inconsistent. Harrison *et al.* (2003) found slightly faster degradation of the S-isomer in aerobic conditions in the landfill plume at Helpston. Zipper *et al.* (1998) also found a seven-fold excess in the R-isomer compared to the S-isomer in the landfill plume at Kollikken, Switzerland. Conversely, Rugge *et al.* (2002) observed no differential degradation of R or S-isomers within the aerobic field injection trial at Vejen in Denmark whilst Harrison *et al.* (2003) found that only the R-isomer was degraded in anaerobic nitrate-reducing microcosms at Helpston.

6.3.4 Stable carbon isotope fractionation during biodegradation

In biological systems isotopic fractionation commonly occurs between the reactants and products during biodegradation. Changes in carbon isotope ratios invariably mean that a reaction is microbially mediated since in nature only biological transformations produce such large stable isotope fractionations Williams *et al.*, 2001). Stable carbon isotope ratios in mecoprop isomers in groundwater samples collected at Helpston were studied by Williams *et al.* (2001). Isotope ratios could only be obtained for samples with significant concentrations of organic carbon or mecoprop. They found that overall the stable carbon isotope ratio ($\delta^{13}\text{C}$) changed very little and differences between each enantiomer were no more than 1.14 ‰. They concluded that the relatively small changes in $\delta^{13}\text{C}$ made the use of this technique very difficult to apply in elucidating biodegradation, especially given the inherent uncertainty associated with the landfill sources and migration pathways.

6.3.5 Transformation products of mecoprop degradation in aquifers

Baun *et al.* (2003) identified 4-CMP as a potential metabolite of mecoprop in an anaerobic landfill plume, but concluded that the presence of this compound could not be interpreted as conclusive evidence of mecoprop biodegradation. It is possible that it may have been a contaminant in the original herbicide product and 4-CMP was also historically used as a pesticide in its own right.

Reitzel *et al.* (2004) reviewed the potential for using the degradation products of phenoxy acids as evidence for natural attenuation of phenoxy acids in groundwater. Their literature review of production history and degradation pathways for phenoxy herbicides demonstrated that the metabolites of the herbicides are also impurities in the products, making the presence of the compounds *per se* of little use as indicators of degradation. The impurities can make up more than 30% of the herbicide products, particularly from historic sources. Reitzel *et al.* (2004) suggested that impurity/parent herbicide ratios may usefully be used as degradation indicators by comparing the ratio in the groundwater to the 'worst case' ratio in the herbicide product.

Reitzel *et al.* (2004) interpreted lab results as showing no accumulation of mecoprop metabolites in aerobic or anaerobic microcosms. In contrast, Harrison *et al.* (2003) showed that anaerobic transformation led to the transient formation of 4-CMP and this persisted until all of the R-mecoprop had been converted to 4-CMP. This could lead to concerns where anaerobic groundwater leaches into surface water bodies since 4-CMP is very toxic to aquatic organisms (Harrison *et al.*, 2003).

6.3.6 Factors controlling mecoprop degradation in aquifers

The literature review shows that mecoprop will sometimes be degraded in some aquifers, but from the studies undertaken there are insufficient data to accurately predict when and at what rate degradation will occur.

The environmental factors that influence the rate of mecoprop degradation in groundwater have not been extensively studied but are likely to be similar to those controlling degradation in topsoil (see Section 4.3). Conditions specifically studied in groundwater are discussed below.

Redox conditions

Mecoprop degradation has not been observed in methanogenic or sulphate-reducing aquifer environments. Limited degradation has been observed in nitrate-reducing environments (Larsen and Aamand, 2001; Harrison *et al.*, 2003; Tuxen *et al.*, 2003; Reitzel *et al.*, 2004). Harrison *et al.* (2003) reported that only the R-isomer was degraded under nitrate-reducing conditions. Enantiomeric analysis was not included in the other studies that demonstrated mecoprop degradation in anaerobic conditions.

Degradation is usually (but not always) observed in aerobic environments.

Oxygen concentration

In laboratory experiments Rugge *et al.* (2002) found decreased lag times and increased aerobic degradation rates with higher oxygen concentrations. Rietzel *et al.* (2004) also observed shorter lag times in samples at higher oxygen concentrations.

Nitrate concentration

Mecoprop degradation has been demonstrated under nitrate-reducing conditions. Harrison *et al.* (2003) observed mecoprop degradation in nitrate-reducing environments, and in samples from an iron-reducing environment following the addition of nitrate to the sample. Elsewhere, Larsen and Aamand (2001) observed some mecoprop degradation under denitrifying suboxic conditions at a nitrate concentration of 64.8 mg/l the groundwater. Tuxen *et al.* (2003) also postulated anaerobic mecoprop degradation in a nitrate-reducing landfill plume in an area with high background nitrate concentrations (35 mg/l).

Therefore, where nitrate is the main respiratory substrate supporting mecoprop biodegradation in groundwater, the extent of attenuation may be controlled by the concentration of nitrate.

Aquifer pH

The Danish sandy aquifers in which mecoprop degradation has been extensively studied are typically acid (pH 5.3 - 6.4) and Johnson *et al.* (2003) have hypothesised that mecoprop degradation in groundwater may be dependent on low pH. Johnson *et al.* (2003) however found that mecoprop could be degraded in groundwater samples from Triassic sandstone with pH values around 7.7, suggesting that low pH is not an obligatory factor for mecoprop degradation, although it may affect (increase) its rate.

Previous exposure of the aquifer to mecoprop

Klint *et al.* (1993) observed that, in laboratory microcosms, repeated spikes of mecoprop were degraded very rapidly without a lag phase. Harrison *et al.* (1998) noted that lag times in the aerobic microcosms at Helpston were much shorter than other studies in previously unpolluted aquifers (e.g., Heron and Christensen, 1992; Agertved *et al.*, 1992).

Torang *et al.* (2003) took samples from the Vejen aquifer following the field injection studies, where previous aquifer exposure could be quantified. They found that previous exposure of the aquifer to mecoprop resulted in reduced or no lag time before the onset of rapid degradation. The effect depended on the amount of previous exposure, for example no lag time was apparent for aquifer sediments previously exposed to mecoprop concentrations greater than 100 µg/l, whereas a lag-time was still observed in aquifer sediments previously exposed to between 10 and 100 µg/l.

Mecoprop concentration

Mecoprop concentration is likely to play an important role in the rate of degradation (Agertved *et al.*, 1992; Albrechtsen *et al.*, 2001; Environment Agency, 2002), and most recent laboratory aquifer studies have deliberately been undertaken at mecoprop concentrations thought to be representative of aquifer conditions (less than 50 µg/l).

Specific studies of the effect of concentration (Torang *et al.*, 2003) have been hampered by difficulties in reproducing mecoprop degradation in previously unexposed aquifer samples at concentrations between 0.025 µg/l and 100 µg/l. Torang *et al.* (2003) did, however, observe for pre-exposed samples that mecoprop degradation at concentrations below 10 µg/l followed first order non-growth kinetics. Above 10 µg/l, the biodegradation rate accelerated gradually due to selective growth of specific biomass. The enhanced rate of degradation by adapted systems was maintained throughout degradation, even at very low residual concentrations (<0.1 µg/l).

7 CONCLUSIONS AND GUIDANCE

Mecoprop is a widely used pesticide that can enter the subsurface environment as a result of normal use, waste disposal and other operations. It can enter subsoil and groundwater as a result of surface application, leakage from landfills and from other operations.

Mecoprop is highly water-soluble and subject to relatively little retardation by sorption processes. It is therefore subject to relatively rapid transport in soil pore water and groundwater. The compound is chemically stable in the subsurface environment but biodegradation can be significant, particularly under aerobic conditions, which will be particularly prevalent in well-drained (and biologically active) topsoils. Consequently, mecoprop applied to topsoil may be highly influenced by precipitation patterns immediately following application - if there is heavy rainfall soon after application then it is likely to be leached to deeper subsoil zones, or groundwater. If there is little precipitation in the first weeks after application then agricultural applications of mecoprop are likely to be completely removed by biodegradation in the topsoil.

The literature indicates that transport of mecoprop in subsoils and groundwater is generally subject to little retardation. The rate and extent of biodegradation in these environments is highly variable, being particularly poor in subsoils and anaerobic groundwater.

Based upon the literature review, guidance is provided below on reasonable assumptions regarding mecoprop sorption and biodegradation in the assessment of its attenuation in unsaturated subsoil and groundwater under UK conditions. The guidance is designed to provide Environment Agency officers and others with reasonable estimates of the rate of mecoprop attenuation in soil and groundwater under representative conditions. It may be applicable during the assessment of pollution risks from landfills and potentially contaminated land. The Agency will expect site-specific data to be collected where hazardous activities are proposed in sensitive hydrogeological environments; however, the guidance may be applied for the initial phases of risk assessment (risk-screening), where site-specific information is not available.

7.1 Partition Coefficients

Partition coefficients for mecoprop have been obtained for a number of British lithologies and engineered clay liners. In comparison to many other organic pesticides, mecoprop is quite poorly sorbed to such materials. When applied to land it is prone to leaching into controlled waters if there is rainfall prior to full biological degradation in the soil zone. The following points have been identified that should be taken into consideration when applying a partition coefficient for mecoprop in the context of a hydrogeological risk assessment:

- the degree of mecoprop attenuation in a porous media is related to the mineralogy and geochemistry of the material. Proportions of organic matter, clay minerals and iron oxyhydroxides may all have a role to play in determining the amount of sorption.
- experimentally obtained ranges of K_{OC} obtained for mecoprop in soil and aquifers (using the linear organic partitioning model) have different ranges. Both have a lower limit of zero, but the maximum limit for soil (55 ml/g) is much less than that for aquifers (5,700 ml/g). These differences may be due to the different nature of organic matter that has undergone diagenesis. However, these ranges were obtained using few data and there may be considerable uncertainty. Equation 2 may be used to convert K_{OC} values to K_d values for the purposes of a risk assessment.
- a relationship is presented (Equation 3) that may be used to determine if organic carbon dominates the sorption of mecoprop in a lithology, and therefore whether the linear

organic partitioning model ($K_d = K_{OC} \times f_{OC}$) is or is not unnecessarily conservative. If it is likely to be conservative, then use of a simple (experimentally derived) site-specific K_d factor may be more appropriate.

- Sorption of mecoprop to organic-rich materials may be only slowly reversible, at rates that are usually much less than those controlling initial sorption. With site-specific (experimentally derived) justification it may be appropriate to use a decay half-life in the transport equations to simulate the loss of mecoprop by sorption, as well as by degradation.
- The degree of sorption is not related to the enantiomeric fraction of the mecoprop in solution.

Table 7.1 presents guideline K_{OC} values for mecoprop based on the literature reviewed in this report. These may be used with site-specific f_{OC} values for the lithologies present at a site to derive K_d values for mecoprop in risk assessments (Equation 2). Where site-specific values of f_{OC} are unavailable, generic values of f_{OC} , such as those in Table 7.2, may be used for screening assessments.

For the purposes of probabilistic modelling, a K_{OC} range is presented that describes a triangular distribution. A minimum value of zero is used in this distribution as retardation has not always been observed in the field, and the best estimate value is chosen as three to bias values toward the more commonly observed lower part of the range. Full details and guidelines on the use of probabilistic values in risk assessments can be found in Environment Agency (2001a).

Use of a minimum K_d value that accounts for sorption to mineral phases is not recommended at this stage without site-specific data.

Table 7.1 Guideline K_{OC} values for mecoprop

	K_{OC} range ^{1,2} (ml/g)	Comments
Both isomers: soil	0 – 10 – 60	Best estimate value reflects typical measured K_{OC} values. Range includes calculated K_{OC} values
Both isomers: unsaturated zone	0 – 10 – 60, or 0 – 50 – 5700	Use range for soil or aquifer depending on site-specific lithology of the unsaturated zone.
Both isomers: aquifers	0 – 50 – 5700	Best estimate value selected to add some conservatism, given wide range of calculated values.

¹ A triangular distribution is suggested for probabilistic modelling.

² Care should be taken when using estimated K_{OC} values for mecoprop sorption. Reported K_d values (from experimental measurements) for soils range between 0 and 3 ml/g, and between 0 and 0.4 ml/g for aquifer systems. Assessors should consider whether the use of high estimated K_{OC} values produces implausible K_d values.

If site-specific f_{OC} values are unavailable, generic values may be used to derive K_d . Table 7.2 presents some values that might be used. Probabilistic ranges are presented; where two values for f_{OC} are given this indicates that a uniform distribution is suggested, while if three are presented, it is felt that data are of sufficient quality that use of a triangular distribution is justified. Before any generic values are used in a risk assessment, it is strongly recommended that the source reference be examined to ensure that the conditions under which these measurements were made are comparable with the conceptual model of site conditions.

Table 7.2 Ranges of f_{OC} values for selected lithologies (after Steventon-Barnes, 2002)

Lithology / material	f_{OC} range ¹
Upper Chalk	0.000096 – 0.00036 – 0.00065
Middle Chalk	0.00013 – 0.00027 – 0.00068
Lower Chalk	0.00007 – 0.00045 – 0.0012
Oxidised Lincolnshire Limestone	0.0001 – 0.0012 – 0.026
Marl in Lincolnshire Limestone	0.0013 – 0.0044 – 0.015
Unoxidised Lincolnshire Limestone	0.00035 – 0.0031 – 0.027
Triassic Sherwood Sandstone	0.00001 – 0.00028 – 0.00071
Lower Greensand	0.0003 – 0.0004 – 0.0019
Sands and gravels	0.0002 – 0.0017 – 0.012
Silts and clays	0.0006 – 0.0074 – 0.062
Peat	0.099 – 0.24
Oxford Clay	0.005 – 0.048 – 0.17
Kimmeridge Clay	0.01 – 0.21
Lower Lias Clay	0.0026 – 0.074
Lower Coal Measures	0.0038 – 0.022 – 0.073
Glacial Till	0.00033 – 0.0028 – 0.0103 ²

¹ Where two values for f_{OC} are given this indicates that a uniform distribution is suggested for probabilistic modelling; where three are presented then a triangular distribution is suggested.

² Depends on extent of weathering.

7.2 Biodegradation

The scientific literature on mecoprop biodegradation in the unsaturated subsurface and groundwater is relatively limited and indicates great variability in the potential for biodegradation and its rate.

Most of the literature indicates that mecoprop is relatively amenable to biodegradation under aerobic conditions, although some papers have found mecoprop to be persistent. Under anaerobic conditions, biodegradation has been reported for some soil and aquifer samples exhibiting nitrate-, manganese- and iron-reducing conditions but frequently fails to occur. Biodegradation of mecoprop has not been unequivocally demonstrated for sulphate-reducing and methanogenic conditions. Mecoprop may therefore be persistent in many anaerobic environments, such as groundwater pollutant plumes. There is no consistent pattern to the rates of degradation of the different enantiomers of mecoprop. There is no evidence that mecoprop has an inhibitory effect on degradative microorganisms at environmentally relevant concentrations.

Acclimation, over a period of weeks to months, appears to be important in the establishment of a biodegradative population in those environmental samples previously unexposed to mecoprop but degradation capacity appears to persist for significant periods once acclimation has taken place.

The accumulation of 4-CMP as an intermediate during degradation has been reported but this is not an invariable occurrence. Since the 4-CMP compound is highly toxic to aquatic life, it should be included in the dataset generated for the assessment of sites where mecoprop is considered to be a significant component.

Biodegradation in topsoil has been relatively widely studied, with mecoprop half-lives typically being between 10 and 100 days in well-drained, acclimated soils exposed to concentrations of mecoprop that are likely to arise from normal use of the herbicide ($\leq 10 \text{ mg/kg}$;

Smith, 1989). Degradation can be expected to reduce in waterlogged soils due to the development of anaerobic conditions.

There are very few data on the rates of mecoprop degradation in unsaturated subsoils and groundwater in the UK. It is known that there is a very rapid decrease in degradation rate with increasing depth through the soil profile, especially at >1 m bgl. For the UK, no significant degradation was observed in samples from unsaturated Chalk, Triassic Sherwood Sandstone and Lincolnshire Limestone subsoils (Johnson *et al.*, 2000 and 2003). **The Environment Agency therefore recommends that considerable caution should be applied in applying biodegradation as an attenuation mechanism for mecoprop in the unsaturated subsoil (>1 m bgl) component of an initial risk assessment (risk-screening). As a conservative approach, it may be appropriate not to model biodegradation, unless there is site-specific evidence to support this as an attenuation mechanism.**

The interpretation of mecoprop degradation rates in UK aquifers is similarly constrained by a lack of data, with the only significant study being that at Helpston (Lincolnshire Limestone; see Section 6.3). Here, biodegradation was demonstrated to be highly spatially heterogeneous. Under laboratory conditions, mecoprop biodegradation half-lives under aerobic and anaerobic nitrate-reducing conditions could be of the order of tens of days but were significantly greater in some samples. Conversely, Johnson *et al.* (2000, and 2003) detected biodegradation of mecoprop in only a proportion of previously uncontaminated samples collected from the Triassic Sherwood Sandstone aquifer and none at all in samples from the Chalk. Similarly heterogeneous behaviour has been observed elsewhere in Europe. **The Environment Agency therefore recommends that considerable caution should be applied in applying biodegradation as an attenuation mechanism for mecoprop in the groundwater component of an initial risk assessment (risk-screening). As a conservative approach, it may be appropriate not to model biodegradation, unless there is site-specific evidence to support this as an attenuation mechanism.**

The generation of site-specific evidence for mecoprop biodegradation should preferably be based on a ‘lines of evidence’ approach. This involves the collection of data that quantifies the contribution of all processes to the overall attenuation effect, which can indicate the contribution of biodegradation even where it is difficult to measure directly *in situ*. This approach is in accordance with the Environment Agency’s guidance on the evaluation of monitored natural attenuation (Environment Agency, 2000). This approach has been successfully applied in the field to determine mecoprop biodegradation rates (e.g., Tuxen *et al.*, 2003) and to demonstrate where no significant biodegradation took place (e.g., Zipper *et al.*, 1998). The alternative approach is to undertake laboratory testing of biodegradation, which can provide valuable data (e.g., Johnson *et al.*, 2003) but it is difficult to scale laboratory rates to the field.

When biodegradation modelling is justified by site-specific data, there is no clear indication from the literature of the most-appropriate kinetic model. Tuxen *et al.* (2002) noted that Monod kinetics, which incorporates biomass growth, gave a reasonable representation but that first-order kinetics underestimated degradation rate. Fomsgaard (1997) noted that topsoil was best modelled without considering biomass growth, whereas the biomass growth was necessary to obtain a good fit of model predictions with data from deeper (but still ≤1 m) subsoil. These observations may indicate that a kinetic model incorporating biomass growth may be appropriate for environments previously unexposed to mecoprop or nutrient-deficient systems where biomass growth may be necessary to generate an acclimated microbial population but that a non-growth model may be more appropriate for established biodegradative populations.

7.3 Identification of knowledge gaps and research needs

Retardation of mecoprop has been observed in some geological media, yet not in others with comparable organic content. These differences are not fully understood. In addition, no work has been completed to specifically address the possibly key issue of its sorption to inorganic substrates. With the current state of understanding, use of typical linear sorption relationships are conservative, especially for clayey materials such as landfill liners. However, it would be beneficial to address this lack of knowledge in order to improve the quality of landfill risk assessments performed for mecoprop.

Mecoprop biodegradation has been relatively well studied in topsoils, although much of that literature fails to distinguish between biological and other attenuation processes. There is less published research on the rates of mecoprop degradation in unsaturated subsoils and groundwater, which represents a significant gap in our understanding of the fate of this contaminant and prevents the generation of generic guidance. Further experimental studies of mecoprop biodegradation in unsaturated sub-soils and groundwater would be beneficial, particularly were they to address the full range of anaerobic biogeochemical environments that may be encountered in the subsurface. Investigations into the fate of mecoprop metabolites, particularly 4-CMP, would also be helpful in improving the quality of risk assessments performed for mecoprop.

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GLOSSARY OF TERMS

4-CMP	4-chloro-2-methylphenol, otherwise known as 4-chloro-o-cresol, chlorocresol, or PCOP; an impurity within and metabolite of mecoprop. 4-CMP has been determined as a List I substance for the Groundwater Regulations. CAS Registry Number: 1570-64-5.
Abiotic	Reaction that takes place without the involvement of biological activity
Absorption	Diffusion of a molecule or ion into the structure of a porous particle
Acclimation	The physiological process through which an organism grows accustomed to a new environment. In microbial cultures, this can involve enzymatic changes that allow it to use a new nutrient source for energy. Also termed adaptation.
Adaptation	See Acclimation.
Adsorption	Retention of a molecule or ion on the surface of a solid particle
Aerobic	An environment containing oxygen; biodegradation or other process operating in the presence of oxygen
Anaerobic	An environment containing no oxygen; biodegradation or other process operating in the absence of oxygen
Aquifer	Saturated underground rock or sediment formation which is sufficiently permeable to allow the flow of water
Atrazine	A herbicide. 6-chloro-N ₂ -ethyl-N ₄ -isopropyl-1,3,5-triazine-2,4-diamine. Atrazine has been determined as a List I substance for the Groundwater Regulations. CAS Registry Number: 1912-24-9.
bgl	Below ground level
Bioavailability	In situ availability of a chemical to biological processes
Biodegradation	Biological conversion of a contaminant into simpler compounds
BSI	British Standards Institute
Chemical degradation	Chemical conversion of a contaminant into simpler compounds
Chiral	A compound having two mirror image structures which cannot be superimposed
Chiral inversion	Process by which one chiral isomer is converted to the other, also known as enantiomerisation.
Co-metabolism	Fortuitous metabolism of a compound by microorganisms metabolising other compounds. The microorganisms gain no benefit from the co-metabolism.
Connate	Water trapped in a sedimentary deposit when the deposit was laid down
Defra	Department for Environment, Food and Rural Affairs
Denitrification	Anaerobic biological activity utilising nitrate as electron acceptor. The end-product of respiration is usually nitrogen but intermediate formation of nitrite or nitrous oxide may be detected. Also termed nitrate-reduction.

DNOC	A herbicide. 2-methyl-4,6-dinitrophenol.
EF	Enantiomeric fraction
Electron acceptor	Substrate that is reduced during respiration. Common electron acceptors used by micro-organisms include oxygen (in aerobic environments) or nitrate, iron (III), sulphate, manganese (IV) (usually in the absence of oxygen).
Electron donor	Substrate that is used in metabolism to supply electrons to the respiratory chain and is hence oxidised.
Enantiomer	One mirror image form of a chiral compound; also known as a stereoisomer.
Enantiomeric Fraction (EF)	$[R] / ([R]+[S])$ where [R] is the concentration of the R-isomer and [S] is the concentration of the S-isomer
Enantiomerisation	Process by which one chiral isomer is converted to the other, also known as chiral inversion.
Enantioselective	A process by which one enantiomer is selected preferentially
First-order kinetics	A reaction where the rate of reaction is independent of the contaminant concentration.
f_{oc}	Fraction of organic carbon (in aquifer or soil media)
Half-life	The time required for something to decline to half of its initial value. In the context of this report the time taken for the concentration of a contaminant to decline by 50%.
Hydrolysis	A chemical reaction between an organic contaminant and water.
Iron-reduction	Anaerobic biological activity utilising iron (III) as an electron acceptor. The product of respiration is iron (II).
Isoproturon	A herbicide, 3-(4-isopropylphenyl)-1,1-dimethylurea. Isoproturon has been determined as a List II substance for the Groundwater Regulations. CAS Registry Number: 34123-59-6.
IUPAC	International Union of Pure and Applied Chemistry.
K_d	Partition coefficient. The ratio of the activities of a chemical species at equilibrium between two phases (liquid and solid in the context of this report) at a given temperature.
K_{oc}	The partition coefficient between water and organic carbon defined as K_d normalised to the aquifer matrix f_{oc} .
K_{ow}	The octanol-water partition coefficient. A measure of the hydrophobicity of a compound, expressed as the ratio of the concentration of a contaminant in n-octanol to water at equilibrium under defined test conditions.
Lag period	Period during microbial acclimation (q.v.) when microbial degradation does not occur or occurs at a very reduced rate.
Manganese-reduction	Anaerobic biological activity utilising manganese (IV) as an electron acceptor. The product of respiration is manganese (II).
MCPCA	A herbicide (4-chloro-2-methylphenoxy)acetic acid. CAS Registry Number: 94-74-6.

MCPP	Mecoprop; (RS)2-(2-methyl-4-chlorophenoxy) propionic acid. CAS Registry Number: 7085-19-0.
Mecoprop	Herbicide comprising (RS)2-(2-methyl-4-chlorophenoxy) propionic acid, its salts or esters.
Mecoprop-P	Herbicide comprising (R)2-(2-methyl-4-chlorophenoxy) propionic acid, its salts or esters.
Metabolite	A chemical intermediate in metabolic reactions
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.
Nitrate-reduction	See <i>Denitrification</i> .
Oxidation – Reduction	See <i>Redox</i> .
PCOC	Another name for 4-CMP. An impurity within and metabolite of mecoprop
Phenoxy acid herbicide	Group of herbicides with similar chemical structure including mecoprop, MCPA and dichlorprop.
Photodegradation	The process of decomposition of a substance upon exposure to radiant energy such as the action of light.
Preventol-B2	Trade name of a root treatment agent used in bituminous roof sealing membranes in flat roofs; a bi-ester of mecoprop which hydrolyses to mecoprop.
Racemic Mixture	Mixture containing 50% of each enantiomer
Redox	Any reaction which involves the transfer of one or more electrons between chemicals. Microbial respiration is a series of redox reactions.
Retardation	A measure of the reduction in solute velocity relative to the velocity of the advecting groundwater caused by processes such as adsorption.
R-isomer	The 'rectus' or 'right-handed' enantiomer
Saturated zone	The portion of subsurface soil and rock where every available space is filled with water.
S-isomer	The 'sinister' or 'left-handed' enantiomer
Sorption	Generic term describing partitioning processes (e.g. partitioning of a solute between dissolved and solid phases). Applied in this report particularly to the process of attachment to the soil or aquifer matrix.
Stereoisomer	One mirror image form of a chiral compound; also known as an enantiomer.
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 ₂ S or metal sulphide salts.
Unsaturated Zone	The zone between the land surface and the water table. It includes the soil zone, unsaturated rock, and capillary fringe. The pore spaces contain water at less than atmospheric pressure, as well as air and other gases.

Saturated bodies, such as perched groundwater may exist within the unsaturated zone. Also called zone of aeration or vadose zone.

Xenobiotic compound

A compound that does not occur naturally.

Zero-order kinetics

A reaction where the rate of reaction is independent of the contaminant concentration.

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APPENDIX 1. Literature Search Methodology

Literature searching was conducted by use of internet resources and commercial abstracting sources.

Internet resources used included:

www.sciencedirect.com
www.scirus.com
www.epa.gov
www.usgs.gov
www.google.com
www.bgs.ac.uk
www.ingenta.com
www.pesticides.gov.uk
www.geolsoc.org.uk

The following commercial abstracting services were used:

- Cambridge Scientific Abstracts
- ISI Web of Science

The keywords used for the searches were generally as follows (where * is a wildcard to allow inclusion of topsoil, subsoil etc with *soil):

Keyword = (Mecoprop OR MCPP OR 7085-19-0) AND (landfill OR groundwater OR aquifer OR *soil)

Keyword = (Mecoprop OR MCPP OR 7085-19-0) AND (*degradation OR decay)

Keyword = (Mecoprop OR MCPP OR 7085-19-0) AND (*sorption OR attenuation OR retardation)

APPENDIX 2. Literature Review Summary Sheets

Agertved, J., Rügge, K. & Barker, J.F., 1992

Transformation of the herbicides MCPP and Atrazine under natural aquifer conditions.

Injection testing of natural sandy aerobic aquifer in Canada demonstrates mecoprop degradation.

Location	Borden, Ontario, Canada
Zone	Aquifer
Conditions	Continuous injection experiment to aerobic aquifer, <i>in-situ</i> tests and laboratory
Lithology	Sand
Source of Mecoprop	Weekly injections
Mecoprop concentration	400 µg/l
Degradation Rate	Adaptation period / lag period of 42-56 days, followed by transformation from 400 - 30 µg/l. No degradation in <i>in-situ</i> tests or laboratory.
Sorption Data	Mecoprop not retarded relative to chloride.
Enantiomeric Analysis	No.

Albrechtsen H-J., Mills, M, Aamand, J. & Bjerg, P.L., 2001

Degradation of herbicides in shallow Danish aquifers: an integrated laboratory and field study.

Investigations of horizontal and vertical variability of degradation rates from the unsaturated zone to the aquifer.

Location	Vejen, Denmark; Fladaerne Baek and other Danish aquifers
Zone	Unsaturated zone, aquifer
Conditions	Aerobic and anaerobic; batch experiments, column studies, field injection
Lithology	Sand
Source of Mecoprop	Field injection, lab
Mecoprop concentration	Vertical experiment - 10 to 170 µg/l; Horizontal variation - 50 µg/l; Field injection approx 40 µg/l.
Degradation Rate	Vertical experiment, Fladaerne Baek: Aerobic degradation in vertical profile from plough layer to aquifer at 7.7m bgl. Decrease in mecoprop degradation rate with depth - from half life of 19 days at 0.06 mbgl to 1-7 years at 3.4 mbgl. Horizontal experiment: no mecoprop degradation in 8 Danish aquifers, aerobic and anaerobic (371 days). Field injection (Vejen) : MCPP degraded - appears to be 60 day lag period followed by rapid degradation.
Sorption Data	Not discussed
Enantiomeric Analysis	No.

According to Torang (pers. comm.) for other phenoxy acids higher concentrations (10-50 µg/l) seem to be needed for growth dependent degradation. According to Rugge (2002) Raising the oxygen concentration reduced the lag period and increased the degradation of MCPP.

Albrechtsen H.-J., Clausen, L. & Pedersen, P.G., 2003

Degradation of the herbicides atrazine, isoproturon and MCPP in the subsurface at four European sites.

Lab studies of aquifer samples from across Europe to compare with Danish results.

Location	Breville, France; Krauthausen, Germany; Martigny, Switzerland; Havdrup, Denmark.
Zone	Unsaturated zone, aquifer
Conditions	Aerobic and anaerobic; batch experiments
Lithology	Limestone (Breville); otherwise unspecified
Source of Mecoprop	^{14}C labeled mecoprop
Mecoprop concentration	Not specified
Degradation Rate	Not specified; degradation recorded in unsaturated zone (aerobic) in limestone at Breville, decreasing with depth. Mecoprop degradation in 7 out of 8 of aerobic samples but not in anaerobic samples.
Sorption Data	Not discussed
Enantiomeric Analysis	No.

Baun, A., Reitzel, L.A., Ledin, A., Christensen T.H., and P.L. Bjerg, 2003

Natural attenuation of xenobiotic organic compounds in a landfill leachate plume (Vejen, Denmark).

Field evidence for degradation of a wide range of xenobiotic compounds in anaerobic conditions; Comparison with previous studies of leachate plume 10 years after first investigation. No evidence for degradation of Mecoprop.

Location	Vejen, Denmark
Zone	Aquifer
Conditions	Naturally aerobic aquifer; anaerobic conditions in a area of plume downgradient from landfill. Methanogenic 0-40m from landfill; iron reducing conditions predominant >40m from landfill.
Lithology	Sand
Source of Mecoprop	Landfill, mixed waste, 1962-1981
Mecoprop concentration	Up to 600 µg/l at border of landfill; 220 µg/l decreasing to 26 µg/l at 135m from the landfill.
Degradation Rate	No degradation - decrease only by dilution (comparison to chloride as stable tracer)
Sorption Data	Earlier experiments demonstrate sorption is not important.
Enantiomeric Analysis	No

Identified 4-chloro-o-cresol in the plume; may be derived from the degradation of mecoprop, however may also be present as a contaminant in the pesticide. Also indistinguishable from 4-chloro-m-cresol which is a pesticide in its own right. i.e. presence of possible degradation products not conclusive evidence of degradation.

Bjerg, P.L., Bay. H., Rosenborg, B., Albrechtsen, H.-J., Reitzel, L.A., Tuxen, N., Ledin, A. & Hansen, H.P.B., 2003

Degradation of a mixture of phenoxy acids, related chlorophenols and other herbicides at a former machine pool.

Study of former machine pool (site for storage and use of machines).

Location	Bornholm, Denmark
Zone	Aquifer
Conditions	Not defined
Lithology	Not defined.
Source of Mecoprop	Agricultural machine pool dating from 1950s.
Mecoprop concentration	Up to 750 µg/l for a single compound (not necessarily mecoprop)
Degradation Rate	Not defined; evidence for field scale degradation
Sorption Data	Not discussed.
Enantiomeric Analysis	Not presented.

Discussion of presence of impurities in herbicides in old contamination sites - should be included in analysis.

Broholm, M.M., Rügge, K., Tuxen, N., Højbjerg, A.L., Mosbæk, H. & Bjerg, P.L., 2001

Fate of herbicides in a shallow aerobic aquifer: A continuous field injection experiment (Vejen, Denmark).

Location	Vejen, Denmark
Zone	Aquifer
Conditions	Aerobic (2-10 mg/l oxygen); pH 4.3 -7; Temperature 10 degC.
Lithology	Medium - coarse glacio-fluvial sand ($f_{OC} = 0.0001$)
Source of Mecoprop	Field injection at point source
Mecoprop concentration	40 µg/l in groundwater immediately downgradient from injection wells.
Degradation Rate	Mecoprop not degraded in aquifer in first 80-120 days, thereafter rapid degradation to below detection limits within 1m of injection wells, corresponding to hydraulic retention time in aquifer of less than 3 days.
Sorption Data	Negligible retardation.
Enantiomeric Analysis	See Williams <i>et al</i> 2003.

No accumulation of chlorophenols.

Brooke, D. and Matthiessen, P., 1991

Development and validation of a modified fugacity model of pesticide leaching from farmland

Location	Herefordshire, UK
Zone	Soil
Conditions	Aerobic
Lithology	n/a
Source of Mecoprop	Field spraying
Mecoprop concentration	11 µg/l in stream water after 25mm rainfall two days after spraying
Degradation Rate	Declined by half in 3.3 days and by 90% in 25 days
Sorption Data	n/a
Enantiomeric Analysis	n/a

Bucheli, T.D., Müller, S.R., Voegelin, A., Schwarzenbach, R.P., 1998

Bituminous roof sealing membranes as major sources of the herbicide (R,S)-mecoprop in roof run-off waters: potential contamination of groundwater and surface waters.

Field study of the occurrence and behaviour of pesticides in roof runoff; identified up to 500 ug/l mecoprop in roof runoff compared to rainwater; believed to be derived from breakdown of root protection agent Preventol in flat roofs. Comparison of mecoprop loads from flat roofs and agricultural applications in Greifensee area of Switzerland revealed loads of similar order of magnitude.

Location	Greifensee, Switzerland
Zone	Run-off
Conditions	Flat roof run-off
Lithology	n/a
Source of Mecoprop	Preventol B-2 root protection agent in bituminous roof sealing membranes - bi-ester of mecoprop.
Mecoprop concentration	up to 500 µg/l
Degradation Rate	No data
Sorption Data	No data
Enantiomeric Analysis	ER of 0.8 to 1.4

Buser, H-R, and Muller, M D, 1998.

Occurrence and transformation reactions of chiral and achiral phenoxyalkanoic acid herbicides in lakes and rivers in Switzerland.

Location	Switzerland
Zone	Surface Water
Conditions	N/a
Lithology	N/a
Source of Mecoprop	Agricultural run-off (only Mecoprop-P registered for use); possible other unidentified sources
Mecoprop concentration	Well below 100 ng/l
Degradation Rate	No data
Sorption Data	No data
Enantiomeric Analysis	Both enantiomers present. In some lakes observed R > S; in other lakes S > R. Laboratory incubations confirmed significant biologically mediated enantiomerisation leading ultimately to enrichment of S-isomer.

Clausen, L. Fabricius, I.L. & Madsen, L., 2001

Adsorption of pesticides onto quartz, calcite, kaolinite and a-alumina.

Batch experiments of pesticide adsorption to different mineral surfaces.

Location	n/a
Zone	n/a
Conditions	n/a
Lithology	Quartz, calcite, kaolinite, alumina
Source of Mecoprop	Laboratory addition
Mecoprop concentration	0.25 mg/l
Degradation Rate	No data
Sorption Data	Detectable adsorption of anionic pesticides (incl. mecoprop) only measured when positive sites present on the mineral surface. Detectable adsorption of mecoprop onto kaolinite when CaCl_2 was added as an electrolyte.
Enantiomeric Analysis	No data.

de Liphay, J.R., Johnsen, K., Aamand, J., Tuxen, N., Albrechtsen, H-J. & Bjerg, P.L., 2003

Continuous exposure of pesticides in an aquifer changes microbial biomass, diversity and degradation potential.

Comparison of microbial biomass in sediment and groundwater samples collected within and outside the Vejen field injection plume.

Location	Vejen, Denmark
Zone	Aquifer
Conditions	Within and outside field injection plume; aerobic
Lithology	Sand
Source of Mecoprop	Laboratory addition
Mecoprop concentration	Not specified
Degradation Rate	Rapid degradation of mecoprop in samples taken from within the plume; no degradation over 100 days in samples from outside the plume.
Sorption Data	Not discussed
Enantiomeric Analysis	No.

No mecoprop degraders found outside plume, but present in all samples within plume.

de Liphay, J.R., Johnsen, K., Aamand, J., Tuxen, N., Albrechtsen, H-J. & Bjerg, P.L., 2003

In situ exposure to low herbicide concentrations affects microbial population composition and catabolic gene frequency in an aerobic shallow aquifer.

Comparison of sediment and groundwater samples collected within and outside the Vejen field injection plume. Continuous exposure to low herbicide concentrations can markedly change the bacterial composition of a subsurface aquifer.

Location	Vejen, Denmark
Zone	Aquifer
Conditions	Within and outside field injection plume; aerobic
Lithology	Sand
Source of Mecoprop	Laboratory addition
Mecoprop concentration	< 40 µg/l
Degradation Rate	No data.
Sorption Data	Not discussed.
Enantiomeric Analysis	No

Environment Agency, 2004b

Development of the partition coefficient (K_d) test method for use in environmental risk assessments.

Environment Agency R&D Technical Report P1-500/4/TR

Evaluation and development of partition coefficient batch test methodology presented in R&D TR P340 for a wider range of substances. The report described method development and validation, and the results of K_d determination for a range of substances to a siltstone, used to test and validate the method.

Location	Rock samples of Tredorn Slate Formation, Cornwall
Zone	Unsaturated zone
Conditions	Laboratory batch tests, aerobic
Lithology	Siltstone
Source of Mecoprop	Laboratory addition
Mecoprop concentration	50 µg/l
Degradation Rate	No data.
Sorption Data	K_d determinations from batch tests: 0.003 and 0.11 ml/g. Measured foc value for siltstone of 0.0105 (1.05%)
Enantiomeric Analysis	No

Felding, G., 1994

Leaching of phenoxyalkanoic acid herbicides from farmland.

Measurement of acid herbicide concentrations in drainage water from clayey soils in farmland treated with herbicides.

Location	Blans, Falkerslev and Gyldenholm, Denmark
Zone	Topsoil, Subsoil
Conditions	Up to 1.4m below ground level; presume aerobic.
Lithology	Sandy loam over glacial clay; organic carbon content of plough layer ca. 1%
Source of Mecoprop	Agricultural spraying of 'Ester' or 'Salt'; includes information on application rates and timing.
Mecoprop concentration	Blans <0.01 µg/l to 0.14 µg/l; Falkerlev n.d. - 0.34 µg/l; Gyldenholm n.d.
Degradation Rate	None. Ref to half-lives being 4 - 41 days.
Sorption Data	Esters more readily adsorbed than acid. Ref to K_{OC} of mecoprop as 20 ml/g i.e. little sorbed in most soil types because of high polarity and negative charge.
Enantiomeric Analysis	No

Spraying mecoprop salt in spring resulted in leaching of the acid; spraying ester in the autumn did not result in any leaching of the hydrolysed compound. Ester hydrolysis may be slowed by low temperatures, and esters more readily adsorbed into the soil.

Fletcher, C. A., Bubb, J. M., and Lester, J. N., 1995

Agricultural Inputs of Mecoprop to a Salt Marsh System: Its Fate and Distribution Within the Sediment Profile.

Measurement of acid herbicide concentrations in drainage water from agricultural land to salt marsh. Mainly looking at surface run-off and subsequent concentrations in Salt Marsh.

Location	Harwich, Essex, UK
Zone	Topsoil
Conditions	Tidal salt marsh. Samples collected before application on adjacent agricultural land and after first major rainfall event. Soil samples up to 0.5 m below ground level
Lithology	Sandy loam over London Clay
Source of Mecoprop	Agricultural spraying of 'Salt' in spring; includes information on application rates and timing.
Mecoprop concentration	Drainage water: <0.05 µg/l pre-application; max 25.8 µg/l; In salt marsh: pre-application: <0.2 ng/g; max 5.1 ng/g in vegetated marsh and 9.9 ng/g in creek. Found at up to 0.5m depth in marsh (possibly due to burrowing animals?)
Degradation Rate	Reports half life in agricultural soils of 6 -30 days; time between application and first rainfall therefore important in determining impact.
Sorption Data	No data.
Enantiomeric Analysis	No

Fomsgaard, I.S., 1997

Modelling the mineralisation kinetics for low concentrations of pesticides in surface and subsurface soil.

Highly detailed kinetic model based on mineralisation results at low concentrations; ploughed soil and subsoil.

Location	Soils from Denmark, Germany, Spain, Italy
Zone	Topsoil
Conditions	Laboratory
Lithology	Mixed soil and subsoil. Up to 6% humus.
Source of Mecoprop	^{14}C labelled mecoprop added in lab.
Mecoprop concentration	0.04 $\mu\text{g/g}$ for degradation experiments; 5 $\mu\text{g/g}$ for sorption
Degradation Rate	Different kinetics in ploughed soil compared to topsoil. Topsoil best modelled without considering biomass growth, whereas the biomass growth was necessary to obtain a good fit of model predictions with data from deeper ($<=1$ m) subsoil.
Sorption Data	K_d measured as: 0-0.7 ($\mu\text{g/g}/(\mu\text{g/ml})$) where humus <1%; 0.4-0.8 where humus 1-4%; 2.6 - 2.8 where humus ca. 5% (garden soil).
Enantiomeric Analysis	No

Harris, G.L., Nicholls, P.H., Bailey, S.W., Howse, K.R., Mason, D.J., 1994

Factors influencing the loss of pesticides in drainage from a cracking clay soil

UK topsoil field tests; mecoprop completely degraded before drainflow occurred.

Location	Brimstone Farm, Oxfordshire, England
Zone	Topsoil
Conditions	Plot lysimeters.
Lithology	Cracking clayey soil
Source of Mecoprop	Agricultural autumn application
Mecoprop concentration	Not given.
Degradation Rate	T 1/2 4.5 days (reported in Harris <i>et al</i> 2000). Mecoprop not detected in drainflow; dry autumn and 'long' delay between application and onset of drainflow; degradation before drainflow occurred.
Sorption Data	0.61 ml/g (reported in Harris <i>et al</i> 2000)
Enantiomeric Analysis	No

Harris, G.L., Catt, J.A., Bromilow, R.H., Armstrong, A.C., 2000

Evaluating pesticide leaching models: the Brimstone Farm dataset.

UK Plot lysimeter studies of cracking clay soil.

Location	Brimstone Farm, Oxfordshire, England
Zone	Topsoil
Conditions	Plot lysimeters (0.2 hectares)
Lithology	Cracking clayey soil
Source of Mecoprop	Agricultural application - plot 6 residual spring application and autumn application; Plot 9 residual spring application only.
Mecoprop concentration	Spring: mecoprop 1179 g/ha; Autumn mecoprop 2395 g/ha
Degradation Rate	Mecoprop not detected in drainflow; dry autumn and 'long' delay between application and onset of drainflow; degradation before drainflow occurred.
Sorption Data	K_d reported as 0.61 ml/g.
Enantiomeric Analysis	No

Harrison, I., Leader, R.U., Higgo, J.J.W., Williams, G.M., 1998

A study of the degradation of phenoxyacid herbicides at different sites in a limestone aquifer.

Laboratory and borehole microcosm comparison of mecoprop degradation in aerobic and anaerobic conditions.

Location	Helpston, Cambridgeshire, UK
Zone	Aquifer
Conditions	Borehole and laboratory microcosms; aerobic and iron reducing anaerobic
Lithology	Lincolnshire Limestone
Source of Mecoprop	Addition of mecoprop plus other organic contaminants. Mecoprop was also present in the landfill plume.
Mecoprop concentration	Anaerobic microcosm - 7000 µg/l; aerobic microcosm - 2000 µg/l.
Degradation Rate	Anaerobic - no degradation over 140 days; Aerobic lag period of 4 days followed by rapid degradation, below detection limit after 10 days.
Sorption Data	No data
Enantiomeric Analysis	No

Harrison, I., Williams, G.M., Carlick, C.A., 2003

Enantioselective biodegradation of mecoprop in aerobic and anaerobic microcosms.

Location	Helpston, Cambridgeshire, UK
Zone	Aquifer
Conditions	Laboratory microcosms
Lithology	Lincolnshire Limestone
Source of Mecoprop	Landfill: 40 tonnes mecoprop deposited during the 1980s; Laboratory: addition of mecoprop and mecoprop-p
Mecoprop concentration	Within aquifer - Sulphate reducing – 3128 µg/l; Iron reducing 1590 µg/l; aerobic nitrate reducing 684-282 µg/l; aerobic sub-oxic 257 µg/l; within lab samples: nitrate reducing – 500 µg/l to 10,471 µg/l; aerobic up to 15,000 µg/l.
Degradation Rate	No degradation in methanogenic/ sulphate reducing; R isomer degraded in iron reducing (after addition of nitrate and lag period of 21 days) and in nitrate reducing (First order 0.65 mg/l/day); both degraded in aerobic over 6 days (Zero order 1.9 mg/l/day for S isomer, 1.32 mg/l/day R isomer).
Sorption Data	Not discussed
Enantiomeric Analysis	Preferential degradation of S isomer in aerobic conditions (R also degraded); only R isomer degraded in nitrate reducing conditions.

Helweg, A., 1993

Degradation and adsorption of ^{14}C mecoprop (MCPP) in surface soils and in subsoil. Influence of temperature, moisture content, sterilisation and concentration on degradation.

Sorption and degradation data for three different soil types under different conditions.

Location	Flakkebjerg, Roskilde and Jyndevad, Denmark
Zone	Topsoil, subsoil
Conditions	Laboratory; aerobic
Lithology	Sandy loam and coarse sandy soil, 0.3 - 2.6 % humus.
Source of Mecoprop	^{14}C labelled mecoprop
Mecoprop concentration	0.2 to 2 mg/kg
Degradation Rate	Surface soil half-life 1.3 - 20 days depending on conditions; shorter half-life at lower concentrations or higher temperature; longer half life at 5 degrees C; Subsoil half-life 7 days at 0-33 cm, 34 - 70 days at 33cm - 1m. No degradation in sterile soil.
Sorption Data	Surface soils only: K_d 0.07 - 0.2; K_{oc} 8.4, 13.3 and 5.3.
Enantiomeric Analysis	No

Heron, G. and Christensen, T.H., 1992

Degradation of the herbicide mecoprop in an aerobic aquifer determined by laboratory batch studies.

Laboratory aerobic degradation in aquifer samples; results interpreted as indicative of enantioselective degradation.

Location	Vejen, Denmark
Zone	Aquifer
Conditions	Laboratory; aerobic; groundwater and sediment suspension.
Lithology	Sand
Source of Mecoprop	Laboratory
Mecoprop concentration	65, 140, 400 and 1400 µg/l
Degradation Rate	Lag period of 20 to 110 days; then stepwise degradation of 50% of total mecoprop, followed by other 50% - interpreted as enantiomeric effects; total degradation at all concentrations over 200 days; variable degradation rates in samples collected only a few metres apart.
Sorption Data	None
Enantiomeric Analysis	No, but results interpreted as enantiomeric effect.

Højberg, A.L., Christensen, J.L., Engesgaard, P. & Bjerg, P.L., 2000

Quantifying pesticide sorption and degradation parameters: modelling a field injection experiment.

Numerical modelling of Vejen field injection experiment.

Location	Vejen, Denmark
Zone	Aquifer
Conditions	Model
Lithology	Sand
Source of Mecoprop	n/a
Mecoprop concentration	n/a
Degradation Rate	Best fit of model at 5m with lag time of 180 days and first order degradation of DNOC in the order of 0.2 / day.
Sorption Data	Noted inverse relationship between DNOC (a pesticide) sorption and pH i.e. sorption controlled by pH (but may be all pesticides not just mecoprop). Used a distributed K_d in the model.
Enantiomeric Analysis	No

Johnson, A.C., White, C., Lal Bhardwaj, C., 2000

Potential for isoproturon, atrazine and mecoprop to be degraded within a chalk aquifer system.

Laboratory aerobic degradation potential studies of topsoil, unsaturated zone and aquifer, Hampshire Chalk.

Location	Hampshire, England
Zone	Topsoil, unsaturated zone and aquifer
Conditions	Laboratory; aerobic, 20°C
Lithology	Chalk
Source of Mecoprop	Laboratory
Mecoprop concentration	100 µg/l
Degradation Rate	No mecoprop degradation over 200 days of in Chalk in absence of solid matrix; with sterile Chalk; with non-sterile unsaturated zone Chalk and sterile groundwater; with non-sterile saturated zone Chalk and sterile groundwater; Mecoprop degradation only seen in topsoil - half life of 62 days.
Sorption Data	No data.
Enantiomeric Analysis	No

Isoproturon degradation was detected in unsaturated zone and aquifer

Johnson, A.C., White, C., Lal Bhardwaj, C., Dixon, A., 2003

The ability of indigenous micro-organisms to degrade isoproturon, atrazine and mecoprop within aerobic UK aquifer systems.

Laboratory aerobic degradation potential studies of topsoil, unsaturated zone and aquifer, Sherwood Sandstone, Lincolnshire Limestone and Chalk. Unanswered questions: Is pesticide degradation in groundwater dependent on the presence of unique, competent degrading organisms? Or are these organisms present everywhere but subtle aspects of the groundwater chemistry, such as the presence or absence of inorganic nutrients or cometabolites, determine the rate of degradation?

Location	UK
Zone	Topsoil, unsaturated zone, saturated zone
Conditions	Laboratory microcosms, aerobic aquifer; 20 degC
Lithology	Chalk, Sandstone (Sherwood Sandstone), Limestone (Lincolnshire Limestone)
Source of Mecoprop	Laboratory
Mecoprop concentration	100 µg/l
Degradation Rate	Sandstone field site soil T 1/2 = 69 days; limestone field site soil, T 1/2 = <102 days. No degradation potential for mecoprop in the subsurface samples from the field sites over 300 days. Some mecoprop degradation potential in groundwater from nearby boreholes in sandstone aquifer (from graph lag time 50 days, T1/2 40 days)
Sorption Data	No data.
Enantiomeric Analysis	No

Noted that the ability of the groundwater at a field site to degrade a pesticide not related to the performance of the soil above. Note concentrations much lower than Harrison *et al.* Suggestion that hypothesis that low pH is required for mecoprop degradation is unfounded since degradation observed at pH 7.7.

Klint, M., Arvin, E. & Jensen, B.K., 1993

Degradation of the pesticides mecoprop and atrazine in unpolluted sandy aquifers.

Lab study of mecoprop degradation in unpolluted aerobic aquifer.

Location	Vejen, Denmark
Zone	Aquifer
Conditions	Laboratory
Lithology	Sand; FOC 0.16 to 0.28%
Source of Mecoprop	Laboratory
Mecoprop concentration	75 – 300 µg/l
Degradation Rate	Lag of up to 40 days at 10degC and half-lives between 35 and 120 days; mecoprop added after lag time rapidly degraded
Sorption Data	No data
Enantiomeric Analysis	No

Kohler, H-P. E, Nickel, K, Bunk, M and Zipper, C, 1999.

Microbial transformation of the chiral pollutants mecoprop and dichlorprop - The necessity of considering stereochemistry.

Review of primarily biochemical experiments on enantiomeric selectivity of mecoprop degradation.

Location	Laboratory cultures; field data from Kollikon, Switzerland
Zone	Not specified.
Conditions	Not specified.
Lithology	Not specified.
Source of Mecoprop	Laboratory addition to cultures; landfill.
Mecoprop concentration	Not specified.
Degradation Rate	Not specified.
Sorption Data	No data.
Enantiomeric Analysis	Racemic mixture within landfill leachate; sevenfold increase in R-isomer 20-50m from landfill interpreted as preferential degradation of S-isomer.

Transformation products of enzyme reactions include 4-chloro-2methylphenol, pyruvate and succinate.

Kristensen, G.B., Johanessen, H., Aamand, A., 2001

Mineralisation of aged atrazine and mecoprop in soil and aquifer chalk.

Laboratory study of the effect of aging on bioavailability and sorption of mecoprop in topsoil and aquifer chalk.

Location	Drastrup, Denmark
Zone	Topsoil, aquifer
Conditions	Laboratory; presume aerobic
Lithology	1m sandy drift over Chalk ($f_{OC} = 0.013$); near surface Chalk weathered to putty chalk ($f_{OC} = 0.0002$).
Source of Mecoprop	Laboratory
Mecoprop concentration	2.5 mg/kg; total liquid 7ml & 10g soil (=3.57 mg/l)
Degradation Rate	Not discussed
Sorption Data	No sorption of mecoprop observed in either soil or chalk samples.
Enantiomeric Analysis	No

Larsen, L. and Aamand, A., 2001

Degradation of herbicides in two sandy aquifers under redox conditions.

Laboratory study using ^{14}C labelled herbicides in two different aquifers representative of aerobic, denitrifying, sulphate-reducing, and methanogenic conditions. Highest degradation rates observed in aerobic topsoil; within aquifer highest degradation in aerobic zone and none measured in sulphate reducing; slow degradation in anaerobic denitrifying and methanogenic zones. Evidence for inhibition of degradation at an early stage.

Location	Fladerne Creek & Asserbo, Denmark.
Zone	Topsoil, unsaturated zone, aquifer
Conditions	Laboratory; 10 degC; samples collected from aerobic topsoil, aerobic unsaturated zone - aquifer; denitrifying, sulphate-reducing, and methanogenic aquifer conditions; conditions retained in during sampling and transit.
Lithology	Sandy; topsoil 18g/kg TOC; others < 0.4 g/kg TOC.
Source of Mecoprop	Laboratory addition of ^{14}C labelled herbicides.
Mecoprop concentration	Topsoil - 0.45 µg / 6g dry weight soil; aquifer - approx, 25 µg/l
Degradation Rate	Measured as recovery of labelled $^{14}\text{CO}_2$. Topsoil - 41% recovery after 85 days; Aerobic capillary zone - 6.6% after 312 days; Anaerobic denitrifying and methanogenic aquifer - ca. 3% after 312 days; anaerobic sulphate reducing - no mineralisation observed
Sorption Data	No data.
Enantiomeric Analysis	No

Larsen, L, Sorensen, S R and Aamand, J, 2000.

Mecoprop, isoproturon, and atrazine in and above a sandy aquifer: vertical distribution of mineralization potential.

Laboratory study of rate of degradation of radiolabelled mecoprop over a vertical profile from topsoil to a sandy aquifer. Observed mecoprop mineralisation at all depths in aerobic conditions, with higher rate of mineralisation in topsoil compared to within aquifer. Also observed evidence for limited anaerobic degradation of mecoprop in nitrate reducing environment.

Location	Fladerne Creek, Denmark
Zone	Topsoil, subsoil and aquifer
Conditions	Lab mineralisation studies; aerobic and anaerobic (with added nitrate); 10 degC.
Lithology	Topsoil ($f_{OC} = 0.026$); sandy subsoil and sandy aquifer.
Source of Mecoprop	Laboratory addition of radiolabelled mecoprop. No previous agricultural use of mecoprop at site, but phenoxy acids detected in up-gradient shallow groundwater.
Mecoprop concentration	8 to 71 $\mu\text{g/l}$ mecoprop.
Degradation Rate	Aerobic: mineralisation observed without lag phase in all samples - topsoil - half life of 19 days at 0.06 mbs and 28 days at 0.3 mbs; subsoil - 139 days at 1.7 mbs; aquifer (below 3.4 mbs) - 1-7 years. Anaerobic - 3.3% of added mecoprop recovered as $^{14}\text{CO}_2$ after 312 days.
Sorption Data	No data.
Enantiomeric Analysis	None

Leistra, M., and Boesten. J.J.T.I, 1989

Pesticide contamination of groundwater in Europe.

Collation of groundwater data. The concentrations of Mecoprop in deep groundwater ranged up to 0.6 g/l.

Location	Western Europe
Zone	Aquifer
Conditions	Multiple, not specified.
Lithology	Multiple
Source of Mecoprop	Not specified
Mecoprop concentration	Up to 0.6 g/l
Degradation Rate	Not discussed
Sorption Data	Not discussed
Enantiomeric Analysis	No

Lyngkilde J., and Christensen, T.H., 1992

Fate of organic contaminants on the redox zones of a landfill leachate pollution plume (Vejen, Denmark).

General study of organic degradation within landfill plume; mecoprop notably more persistent than other compounds.

Location	Vejen, Denmark
Zone	Aquifer
Conditions	Aquifer, anaerobic leachate plume - first 20m methanogenic/sulphidogenic, ferrogenic from 20m to 100m plus
Lithology	Sand
Source of Mecoprop	Landfill; point source
Mecoprop concentration	Not given.
Degradation Rate	Not given, but of the specific organic compounds 'only MCPP migrates further' than 100m
Sorption Data	No data.
Enantiomeric Analysis	No

See later Vejen papers.

Madsen, L., Lindhardt, B., Rosenberg, P., Clausen, L. & Fabricius, I.L., 2000

Pesticide sorption by low organic carbon sediments: a screening for seven herbicides.

Study of sorption of pesticides in 10 Danish aquifer sediments.

Location	Denmark
Zone	Aquifer
Conditions	Aquifer
Lithology	Carbonate free sand, carbonate bearing sand, chalk; f_{OC} less than 0.001.
Source of Mecoprop	Laboratory
Mecoprop concentration	0.25 mg/l
Degradation Rate	Not discussed
Sorption Data	Sorption of mecoprop depends largely on pH, higher at low pH (<6.7) compared to high pH (>7.4). Expect pH to be an influence because it affects both the surface charge of the rock forming minerals, and the degree of dissociation of the carboxylic acid group. Sorption capacity for chalk aquifers is higher than for sandy aquifers for pH=6. K_d ranges from 0.07 to 0.26 ml/g.
Enantiomeric Analysis	No

Muller, M.D., Buser, H-R., 1997

Conversion reactions of various phenoxyalkanoic acid herbicides in soil. 1. Enantiomerisation and enantioselective degradation of the chiral 2- phenoxypropanoic acid herbicides.

Laboratory study of relative degradation rates in topsoil of racemic mecoprop, R-isomer and S-isomer. Also observed biologically mediated chiral conversion (enantiomerisation).

Location	Waderswil, Switzerland
Zone	Topsoil
Conditions	Lab mineralisation studies; aerobic, 20 - 23deg C; included sterilised control samples
Lithology	Garden soil; sandy loam; $f_{OC} = 0.016$.
Source of Mecoprop	Laboratory addition of racemic mecoprop, and enantiopure R-mecoprop and S-mecoprop.
Mecoprop concentration	1mg/l mecoprop.
Degradation Rate	Non-sterile samples - ready degradation of all compounds, half lives 3.9 to 10 days; two phases of degradation with initial linear phase followed by more rapid degradation. Slower degradation of R isomer compared to S isomer. Enantiopure experiments showed evidence of enantiomerisation i.e. appearance of alternative isomer, followed by subsequent degradation. Sterile samples - non-enantio selective degradation observed (half-life 24 - 27 days) with no enantiomerisation.
Sorption Data	No data.
Enantiomeric Analysis	Evidence for biologically mediated enantiomerisation and for faster degradation of S-isomer.

Nilsson, B., Dahl, M., Juhler, R.K., Hoffmann, C.C. & Engesgaard, P., 2000

Fate of two pesticides in a freshwater wetland: comparison of field injection and laboratory results.

Field injection of mecoprop and isoproturon into groundwater discharging to freshwater wetland site.
Implication of significant adsorption but little information on organic matter content.

Location	Voldby, Denmark
Zone	Hillslope soil, wetland
Conditions	Aerobic, anaerobic
Lithology	Not defined
Source of Mecoprop	Field injection, laboratory studies
Mecoprop concentration	33.3 mg/l at field injection site.
Degradation Rate	No degradation within the residence time of 20-40days in lab experiments, aerobic and sulphate reducing.
Sorption Data	Mecoprop attenuated by 25 to 75% compared to bromide (mass retrieval); batch experiments indicate 90 - 95% of pesticide adsorbed irreversibly after a few hours to a few days.
Enantiomeric Analysis	No

Nitschke, L. Wilk, A., Schüssler, W., Metzner, G. and Lind, G., 1999

Biodegradation in laboratory activated sludge plants and aquatic toxicity of herbicides.

Study of biodegradation and aquatic toxicity of herbicides in sludge. Found mecoprop could be degraded in sludge but significant adaptation time (lag time) meaning that short term high doses to waste water treatment plants are unlikely to be degraded. Toxicity tests showed that neither mecoprop nor mecoprop degradation products inhibited the tested aquatic organisms (Daphnia and lemlna).

Location	Germany
Zone	Waste water treatment plants / sludge
Conditions	Aerobic
Lithology	n.a.
Source of Mecoprop	Laboratory addition.
Mecoprop concentration	1 mg/l inflow concentration
Degradation Rate	Lag time 10-15 days; total degradation by 35 days.
Sorption Data	No data.
Enantiomeric Analysis	No.

Pedersen, P.G., Mosbæk, H. & Albrechtsen, H-J., pers. comm.

Fate of eleven pesticides: Degradability and Sorption in eight Danish Aerobic and Anaerobic Aquifers.

Degradation and adsorption study of Danish aquifer sediments.

Location	Multiple, Denmark
Zone	Aquifer
Conditions	Aerobic, denitrifying, manganese and iron reducing, sulphate reducing and methane producing
Lithology	Multiple
Source of Mecoprop	Laboratory
Mecoprop concentration	50 µg/l
Degradation Rate	None observed over 371 days. Concentration decrease in some samples attributed to sorption.
Sorption Data	Average K_d 0.4 ml/g. No aquifer specific data.
Enantiomeric Analysis	No.

Reitzel, L.A., Tuxen, N., Ledin, A., Bjerg, P.L., 2004

Can degradation products be used as documentation for natural attenuation of phenoxy acids in groundwater ?

Literature review of mecoprop degradation and production history; mecoprop metabolites are major impurities in pesticide products. Impurity / parent herbicide ratios may be applicable to demonstrate degradation. Microcosm / field experiments at two sites

Location	Sjoelund and Bornholm, Denmark
Zone	Aquifer
Conditions	Bornholm - nitrate and iron reducing; Sjoelund - nitrate and manganese reducing to aerobic: lab - aerobic , Mn reducing and nitrate reducing
Lithology	Bornholm: moraine clay and silt underlain by sandstone; Sjoelund: sand and gravel
Source of Mecoprop	Bornholm: agricultural machine pool; Sjoelund: landfill
Mecoprop concentration	Bornholm: 15 - 80 µg/l; Sjoelund: <1 - 12 µg/l; added 2.5 µg/l ¹⁴ C labelled
Degradation Rate	¹⁴ C mecoprop totally degraded in all experiments. Lag phases 15 - 160 days; earlier degradation in microcosms with higher oxygen contents.
Sorption Data	No evidence of sorption
Enantiomeric Analysis	No.

Lab results show no accumulation of mecoprop metabolites in microcosms.

Roeth, F.W., 1984

Enhanced herbicide degradation in soil with repeat application.

Review of enhanced degradation with repeat application from the view of negative impact on herbicide effectiveness. Mecoprop one of 70 pesticides considered.

Location	Multiple - review paper
Zone	Topsoil
Conditions	n/a
Lithology	n/a
Source of Mecoprop	n/a
Mecoprop concentration	n/a
Degradation Rate	No specific data.
Sorption Data	No data
Enantiomeric Analysis	No

Romero E., Dios, G., Mingorance, M.D., Matallo, M.B., Pena, A., Sanchez-Rasero, F., 1998

Photodegradation of mecoprop and dichlorprop on dry, moist and amended soil surface exposed to sunlight.

Study of photodegradation of mecoprop. In dry soils, photodegradation at the surface may dominate other transformation pathways. Also plays an important role in first two days of exposure on moist soils.

Location	Vega de Granada, Spain
Zone	Topsoil surface
Conditions	Laboratory, surface aerobic; dry to moist
Lithology	Calcareous soils: Silty loam (2.1% OM), sandy loam (1.5% OM) and clay loam (1.4% OM); Each also amended with 10% peat comprising 78.5% OM.
Source of Mecoprop	Lab addition of mecoprop.
Mecoprop concentration	1 µg/g dry soil (similar to field dosage)
Degradation Rate	Half-life 14 -15 days in dry silty loam and clay loam; < 10 days in sandy loam; Half-life 15-50 days in peat amended soils. Half-life 7-13 days in moist soils but also observed in dark control samples implying biodegradation is also occurring.
Sorption Data	No data
Enantiomeric Analysis	No

Romero, E., Matallo, M.B., Pena, A., Sanchez-Rasero, F., Schmitt-Kopplin, Ph., Dios, G., 2000

Dissipation of racemic mecoprop and dichlorprop and their pure R-enantiomers in three calcareous soils with and without peat addition.

Comparison of degradation of racemic mixture and pure R enantiomer in three calcareous soils with and without the addition of peat. Different enantiomeric effects were observed in each soil, changed by addition of peat.

Location	Vega de Granada, Spain
Zone	Topsoil
Conditions	Laboratory; presume aerobic
Lithology	Calcareous soils: Silty loam (2.1% OM), sandy loam (1.5% OM) and clay loam (1.4% OM); Each also amended with 10% peat comprising 78.5% OM.
Source of Mecoprop	Lab addition of racemic mecoprop and mecoprop-p (R-isomer)
Mecoprop concentration	1 µg/g dry soil (similar to field dosage)
Degradation Rate	See tables (separate sheet); note that this does not include sorption i.e. less dissipation in organic enriched material may be because of higher adsorption.
Sorption Data	No data
Enantiomeric Analysis	R isomer degraded faster in sandy loam and silty loam; S isomer degraded faster in clay loam; Williams et al suggest that adding peat to clay may have made it nitrate reducing

Rügge, K., Bjerg, P.L., Mosbæk, H., and Christensen, T.H., 1999

Fate of MCPP and Atrazine in an Anaerobic Landfill Leachate Plume (Grindsted, Denmark).

Assessment of mecoprop degradation relative to bromide tracer in anaerobic landfill plume by field injection, in-situ microcosm and lab batch tests; found no degradation or sorption.

Location	Grindsted, Denmark
Zone	Aquifer
Conditions	Landfill plume, anaerobic; 10 degC; Mainly iron-reducing; methanogenic close to injection wells; Filed injection studies, in-situ microcosms and laboratory batch studies
Lithology	Medium - coarse grained sand and gravel; FOC 0.01- 0.03%
Source of Mecoprop	Addition of mecoprop plus other organic contaminants. Note pesticides were not observed in the plume, but traces of compounds which could be degradation products of chlorinated phenoxy acids were detected.
Mecoprop concentration	150 µg/l
Degradation Rate	No degradation cf. bromide observed in field injection tests, in-situ microcosms or lab batch tests.
Sorption Data	No significant sorption of mecoprop compared to bromide could be detected.
Enantiomeric Analysis	No

Rügge, K., Juhler, R.K., Broholma, M.M., Bjerg, P.L., 2002

Degradation of the (R)- and (S)-enantiomers of the herbicides MCPP and dichlorprop in a continuous field-injection experiment.

Field injection study of aerobic aquifer; degradation of mecoprop after a lag period, no enantioselectivity observed.

Location	Vejen, Denmark
Zone	Aquifer
Conditions	Field injection, samples taken 1m and 15m from injection wells
Lithology	Glacio-fluvial sand
Source of Mecoprop	Field injection over 7 months of 1000 µg/l racemic mecoprop, diluting to 40 µg/l in the groundwater.
Mecoprop concentration	40 µg/l in groundwater immediately downgradient from injection wells
Degradation Rate	Lag period 60-80 days, followed by degradation to below detection limits at 106 - 132 days. No differential degradation between R & S isomers.
Sorption Data	Not discussed
Enantiomeric Analysis	Yes; no differential degradation between R and S isomers.

Smith, A.E., 1989

Degradation, fate and persistence of phenoxyalkanoic acid herbicides in soil. Mainly considers other herbicides with limited reference to mecoprop.

Location	Saskatchewan, Canada
Zone	Topsoil
Conditions	Laboratory; Various
Lithology	Clay, clay loam and sandy loam; OM 2 - 11.7 %
Source of Mecoprop	Laboratory
Mecoprop concentration	2 - 15 mg/kg
Degradation Rate	Mecoprop half life 3 - 10 days. Review of phenoxy acid herbicide breakdown suggests first order kinetics (no lag period) below about 10 mg/kg, adaptation and increased breakdown following a lag period at concentrations 10 - 500 mg/kg. Increased degradation rates observed in pre-exposed soils.
Sorption Data	No data for mecoprop. Adsorption of other phenoxyalkanoic acids correlates with soil organic matter content. Adsorption to organic matter unlikely to seriously affect degradation, confirmed by lab experiments showing breakdown of herbicides similar in soils ranging in organic matter from 4 to 12%.
Enantiomeric Analysis	None

Phenoxy acid herbicide breakdown not generally affected by presence of other herbicides.

Tett V.A., Willetts, A.J., and Lappin-Scott, H.M., 1994

Enantioselective degradation of the herbicide mecoprop by mixed and pure bacterial cultures.

Laboratory aerobic degradation of topsoil cultures; only R isomer degraded.

Location	UK
Zone	Topsoil
Conditions	Laboratory; Aerobic
Lithology	Not given
Source of Mecoprop	Laboratory
Mecoprop concentration	Not given
Degradation Rate	No rates. Only R-isomer degraded; faster degradation after prolonged incubation
Sorption Data	Not reported
Enantiomeric Analysis	Only R isomer degraded (aerobic)

Toräng, L., Nyholm, N. & Albrechtsen, H-J., 2003

Shifts in biodegradation kinetics of the herbicides MCPP and 2,4-D at low concentrations in aerobic aquifer materials.

Study of biodegradation kinetics at very low concentrations.

Location	Vejen, Denmark
Zone	Aquifer
Conditions	Laboratory; Aerobic
Lithology	Sand
Source of Mecoprop	Laboratory addition ^{14}C labelled mecoprop
Mecoprop concentration	0.025 – 100 $\mu\text{g/l}$
Degradation Rate	No degradation over 100 days at any concentration in previously unpolluted aquifer; Rapid degradation at 100 $\mu\text{g/l}$ in previously heavily exposed aquifer, no lag time; Lag time of 35 days followed by rapid degradation at 100 $\mu\text{g/l}$ in previously lightly exposed aquifer; at concentrations below 10 $\mu\text{g/l}$ no adaptation observed i.e. little degradation in low exposure sample and no sharp increase in degradation rate in higher exposed sample. Other experiments showed degradation rates linked to previous exposure regardless of added concentration.
Sorption Data	Not discussed
Enantiomeric Analysis	No

Tuxen, N., Tüchsen, P.L., Rügge, K., Albrechtsen, H-J. & Bjerg, P.L. 2000

Fate of seven pesticides in an aerobic aquifer studied in column experiments.

Location	Vejen, Denmark
Zone	Aquifer
Conditions	Laboratory
Lithology	Sand
Source of Mecoprop	Laboratory
Mecoprop concentration	25 µg/l
Degradation Rate	Lag period 16-33 days; half life ca. 16 days at 10degC; zero order degradation rate constant 1.3 - 2.6 µg/l/day.
Sorption Data	Very low sorption of mecoprop. K_d 0 to 0.04
Enantiomeric Analysis	No

Tuxen et al., 2002

Effect of Exposure History on Microbial Herbicide Degradation in an Aerobic Aquifer Affected by a Point Source.

Assessment of effect of previous exposure to mecoprop on degradation potential of samples from aerobic aquifer. Demonstrated relationship between previous exposure to herbicides and percent degraded after 50 days. Lag period reduced. Concluded that there is a spatial variation in the degradation potential of pristine aquifers, as previously observed by others.

Location	Vejen, Denmark
Zone	Aquifer
Conditions	Laboratory microcosms using field samples from Vejen field injection site. Aerobic (7-9 mg/l oxygen), pH 5-5.5. Field samples taken from locations with varying exposure history to mecoprop, based on results of previous monitoring.
Lithology	Medium - coarse glacio-fluvial sand; 0.1 mg C/g dw). GW 4.5 m below ground level
Source of Mecoprop	Lab addition.14C labelled mecoprop
Mecoprop concentration	25 µg/l
Degradation Rate	Variable. Found that Monod kinetics, which incorporates biomass growth, gave a reasonable representation but that first-order kinetics underestimated degradation rate.
Sorption Data	Not discussed
Enantiomeric Analysis	No

Tuxen, N., Ejlskov, P., Albrechtsen, H.-J., Reitzel, L.A., Pedersen, J.K., Bjerg, P.L, 2003

Application of natural attenuation to ground water contaminated by phenoxy acid herbicides at an old landfill in Sjoelund, Denmark.

Laboratory and field study of mecoprop behaviour in landfill plume. Relationship between increasing oxygen content and decreasing phenoxy acids indicating aerobic degradation as a major mass removal process. Presence of putative anaerobic metabolites suggest anaerobic degradation may be taking place in the plume; supported by degradation in anaerobic microcosm.

Location	Sjoelund, Denmark
Zone	Aquifer
Conditions	Field and Laboratory; Landfill in aerobic aquifer; anaerobic conditions in plume; lab microcosms and groundwater sampling
Lithology	Glacial outwash sand/gravel; no liner
Source of Mecoprop	Old landfill; Filled from 1965 to 1975.
Mecoprop concentration	up to 65 µg/l in groundwater
Degradation Rate	Field: Mass loss cannot be explained by dilution; suggestion of degradation within anaerobic as well as aerobic zone. Lab: Aerobic degradation of mecoprop after short lag phase (ca 20 days); anaerobic degradation of mecoprop after long lag phase (ca. 120 days)
Sorption Data	Max K_d of 1.2 used in calculations.
Enantiomeric Analysis	No

Vink, J.P.M. and Van der Zee, S.E.A.T.M, 1997

Pesticide biotransformation in surface waters: multivariate analyses of environmental factors at field sites.

Biodegradation in surface waters at varying locations within a field site. Found large variations in degradation rate. Mecoprop degradation apparently highly sensitive to composition of water samples. Most persistent mecoprop where lowest nitrate nitrogen concentration (0.9 and 0.7 mg N/l).

Location	Lake Markermeer, Netherlands
Zone	Surface Water
Conditions	Surface water; aerobic 1.7 - 10.8 mg/l dissolved oxygen
Lithology	
Source of Mecoprop	Lab addition
Mecoprop concentration	?1mg/l
Degradation Rate	3 - 1400 days
Sorption Data	Not discussed
Enantiomeric Analysis	No

Williams, G.M., Harrison, I., Carlick, C.A., Crowley, O. 2003

Changes in enantiomeric fraction as evidence of natural attenuation of mecoprop in a limestone aquifer.

Comprehensive analysis of groundwater at varying redox conditions within plume associated with Helpston landfills, including enantiomeric analysis and stable isotope analysis. Also laboratory microcosm experiments under similar range of conditions.

Location	Helpston, Cambridgeshire, UK
Zone	Aquifer
Conditions	Field and laboratory; field outside plume - aerobic evolving to sulphate reducing; field within plume: methanogenic/sulphate reducing, iron-reducing, nitrate reducing and aerobic/sub-oxic; within lab used crushed limestone which had been suspended in boreholes within the plume for several months to allow microbial colonisation; methanogenic/sulphate reducing, iron-reducing, nitrate reducing and aerobic.
Lithology	Lincolnshire Limestone
Source of Mecoprop	Landfill: 40 tonnes mecoprop deposited during the 1980s; Laboratory: addition of mecoprop and mecoprop-p
Mecoprop concentration	Up to 39 mg/l in the waste; up to 8 µg/l in the Etton PWS ; Within aquifer - Sulphate reducing - 3128 µg/l; Iron reducing 1590 µg/l; aerobic nitrate reducing 684-282 µg/l; aerobic sub-oxic 257 µg/l; within lab samples: nitrate reducing - 500 µg/l to 10,471 µg/l; aerobic up to 15,000 µg/l.
Degradation Rate	No degradation in methanogenic/ sulphate reducing; R isomer degraded in iron reducing (after addition of nitrate and lag period of 21 days) and in nitrate reducing (First order 0.65 mg/l/day; both degraded in aerobic over 6 days (Zero order 1.9 mg/l/day for S isomer, 1.32 mg/l/day R isomer).
Sorption Data	Not discussed
Enantiomeric Analysis	Preferential degradation of S isomer in aerobic conditions (R also degraded); only R isomer degraded in nitrate reducing.

In field observed predominance of S isomer in nitrate containing samples, with lab results suggest nitrate acts as electron acceptor. In aerobic zone observed increase in proportion of R isomer, which could be explained by faster degradation of S isomer.

Zipper, C, Nickel, K, Angst, W and Kohler, H-P E, 1996.

Complete microbial degradation of both enantiomers of the chiral herbicide mecoprop [(RS)-2-(4-chloro-2-methylphenoxy)propionic acid] in an enantioselective manner by *Sphingomonas herbicidovorans* sp, nov..

Laboratory study of degradation of mecoprop using specific bacterial cultures.

Location	n/a
Zone	n/a
Conditions	Laboratory microbial cultures. Aerobic.
Lithology	n/a.
Source of Mecoprop	Laboratory addition of racemic mecoprop, and enantiopure R-mecoprop and S-mecoprop.
Mecoprop concentration	100 mg/l mecoprop
Degradation Rate	Demonstrated bacterial cultures could utilise mecoprop as sole carbon and energy source
Sorption Data	No data.
Enantiomeric Analysis	In experiments using racemic mecoprop, S-isomer disappeared faster than R-isomer; cells cultured on pure isomers showed preferential metabolism of isomer used in culture. Conclude that enantioselectivity partly the result of the existence of two distinct enzymes.

Zipper, C., Suter, M.J.-F., Haderlein, S.B., Gruhl, M., Kohler, H.P.E., 1998

Changes in the enantiomeric ratio of (R)- to (S)-Mecoprop indicate in-situ biodegradation of this chiral herbicide in a polluted aquifer.

Study of enantiomer ratios in landfill leachate and groundwater; racemic mixture in leachate and predominance of R-isomer; experimental determination of sorption concludes no enantiomeric difference in sorption.

Location	Kolliken, Switzerland
Zone	Aquifer
Conditions	Groundwater; sulphidogenic to methanogenic (natural aquifer aerobic to nitrate reducing)
Lithology	Fractured marls (0.2% OC) and calcareous sandstone (0.3% OC)
Source of Mecoprop	Landfill; chemical waste disposal 1979 to 1985; also lab addition to up-gradient soil samples for sorption assessment.
Mecoprop concentration	up to 124 µg/l in leachate, racemic mixture; <0.001 to 975 µg/l in aquifer, with up to 7 fold excess in R-isomer; Sorption studies 0.182 mg/L and 1.82 mg/L
Degradation Rate	No degradation rates - varying source supply.
Sorption Data	$K_d < 1 \text{ ml/g}$ for sandstone and marl; 20 -36 ml/g for amorphous SiO_2 and montmorillonite; more adsorption at lower concentrations; Calculated retardation factor 1.4. No significant difference between R and S isomers
Enantiomeric Analysis	Preferential degradation of S isomer (aerobic); no preferential adsorption

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