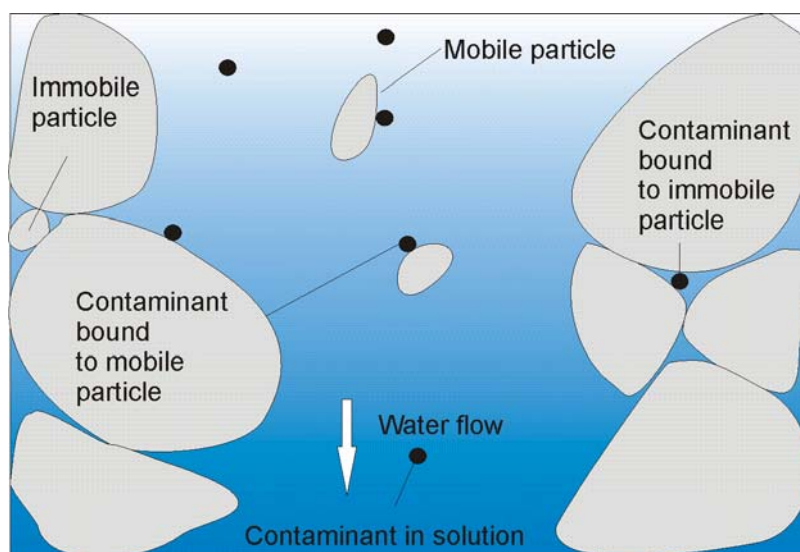




# Colloidal phase transport of pesticides: A review with special reference to major UK aquifers

Groundwater Management Programme  
Internal Report IR/05/131





BRITISH GEOLOGICAL SURVEY

GROUNDWATER MANGEMENT PROGRAMME

INTERNAL REPORT IR/05/131

# Colloidal phase transport of pesticides: A review with special reference to major UK aquifers

D J Lapworth, D C Gooddy, I Harrison, A Kim, C Vane

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# Foreword

This report provides a short review on colloid facilitated transport of contaminants in groundwater as part of the Groundwater Management Programme sub-theme “Colloidal Transport of Pesticides”. The first section introduces the concept of what constitutes colloidal material and briefly describes its sources, occurrence and transport in the environment. The second section concentrates on the interactions between colloids and contaminants and how this enables transport within the environment (with particular reference to pesticides). The third section discusses some examples of pesticide transport in UK aquifer systems and considers the role of colloid facilitated transport using hypothetical scenarios within the framework of a source-pathway-receptor model for pesticides. The methodology for sampling and fractionating colloidal phase material in groundwater is summarised in the last section.

## Acknowledgements

The authors would like to thank BGS and the Groundwater Management Programme for funding the sub-theme 'Colloidal Transport of Pesticides'. Published critical reviews on colloidal transport of contaminants by McCarthy and Zachara (1989) and Ryan and Elimelech (1996) have provided a useful context for this report. The authors thank M Stuart for reviewing the report.

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## Summary

Several studies have highlighted the role of colloids in contaminant transport within the subsurface including notable reviews by McCarthy and Zachara (1989) and Ryan and Elimelech (1996). Colloid facilitated transport of contaminants in the environment has been the subject of intense investigation over the last twenty years. As a result much has been learnt about the formation, and transport of colloids as well as the mode of interaction between colloidal material and contaminants. A large amount of literature exists on colloid facilitated transport of pesticides, but the majority of the work described was laboratory-based study focussed on the soil zone and using isolated humic material. Some recent studies have investigated the transport of colloids in the unsaturated zone, however the issues of heterogeneity and complexities of recharge events are challenges that need further investigation. Few studies have addressed the issue of colloid-facilitated transport of pesticides in groundwater other than to suggest it as potentially significant transport mechanism. This report considers the likely aquifer systems in the UK which may lead to the formation and transport of colloidal material. This may increase the mobility of pesticides from the point of application to groundwater. Methods for sampling and extracting colloids and pesticides from groundwater are also discussed.

# 1 Introduction

## 1.1 WHY COLLOIDAL PHASE TRANSPORT OF PESTICIDES MAY BE IMPORTANT IN GROUNDWATER SYSTEMS

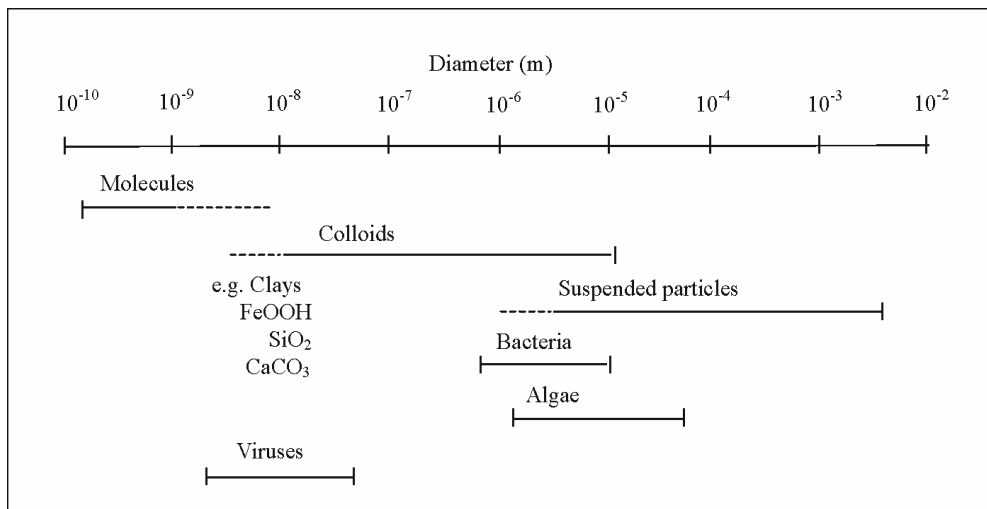
Pesticide detections in groundwaters often show a large degree of temporal variability; concentrations may increase or decrease by up to an order between samples (Gooddy et al., 2001; Lapworth et al., 2006). The reasons for these variations are not fully understood, however, one mechanism that could be contributing is colloidal phase transport. This is due to, among other factors, the following possibilities: sorption to colloids could allow the mobilisation of polar compounds that have low aqueous solubility; particles in the colloidal phase may be able to travel faster than the ‘average’ aqueous phase due to processes such as size-exclusion in the chalk aquifer system; colloidal transport may also be important in rapid by-pass flow, as well as in surface water transport; and diffusion processes may also be limited due the relatively large particle size of colloids leading to less dispersion of pesticides.

## 1.2 COLLOIDAL MATERIAL

Colloids are operationally defined as particles with diameters less than  $10^{-5}$  m (10  $\mu$ m) (Stumm, 1977). These particles can be divided into a number of subsets of different material types that exist in groundwater and other natural environments. Table 1.1 gives a summary of the different types of colloidal material, both organic and inorganic. Figure 1.1 shows where colloidal particles fit in the spectrum of waterborne particles.

Table 1.1 Colloidal material in the environment

<b>Colloidal Particle</b>	<b>Source</b>
Macromolecular dissolved organic carbon: 'humics'	Organic breakdown products and extracellular secretions
Biomolecules (viruses, bacteria etc)	Natural occurrence from soil/groundwater fauna and anthropogenic sources
Microemulsions of nonaqueous phase liquids	Mostly anthropogenic sources
Hydroxides of actinide elements	Mineralisation or contamination
Precipitates of Fe, Mn oxides, silicates and Carbonates	Natural minerals, acid mine drainage
Weathering products and clay fractions	Natural minerals



Source (Stumm, 1977)

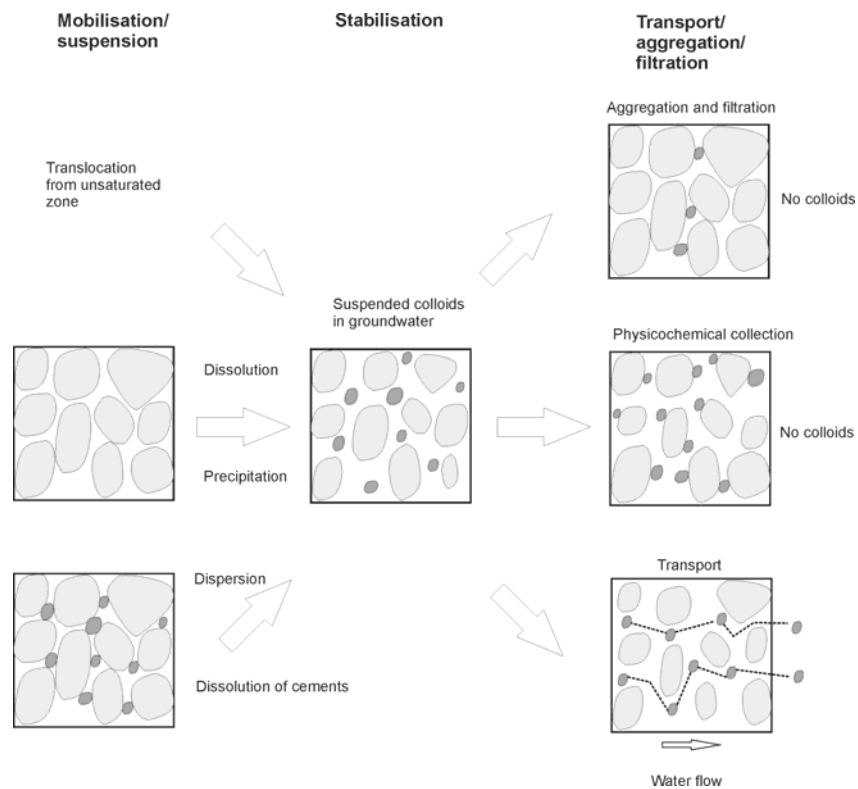
Figure 1.1 Size spectrum of waterborne particles

In reality the distinction between organic and inorganic colloids is over simplistic as colloidal material is often a complex mixture of both, and thus has properties associated with both types of material. Characterising the nature of colloidal material, both its physical structure and the chemical nature of its surface and subsurface is a very active area of research (Buffle and Leppard, 1995a, b; Elimelech et al., 2000). Colloids have a highly heterogeneous surface chemistry in terms of functionality and charge and these properties are often patchwise in nature. Physical characteristics such as surface area, particle size and particle shape are also important factors in controlling colloidal-contaminant interactions and their fate and transport in the environment.

Colloids have been a subject of research for many years and early investigations into the stability of colloids lead to the formation of the 'DVLO' theory in the 1940s. Other early studies focused on the migration of microbial contamination (Keswick et al., 1982). The recognition of the role that colloids play in facilitating contamination migration was highlighted by a number of studies looking at the transport of radionuclides in groundwater (McCarthy and Zachara, 1989; Higgs et al., 1993). There have subsequently been a number of reviews on the importance of colloids in contamination migration (McCarthy and Zachara, 1989; Ryan and Elimelech, 1996; Kretzschmar et al., 1999).

### 1.3 FORMATION, MOBILISATION AND TRANSPORT OF COLLOIDS

Colloids are generated in the soil system by dispersion from soil aggregates in response infiltration and in some cases this can lead to the formation of clay/organic rich horizons in the subsurface (De Jonge et al., 2004a). They are also generated by the decay of organic matter and extracellular excretion of organic molecules from plant and biological material.



Source (McCarthy and Zachara, 1989)

Figure 1.2 Colloidal mobilisation and transport in the subsurface

The source of colloidal material in the saturated zone can be translocation from the unsaturated zone by recharge, in-situ dissolution and precipitation of parent/cemented material, and through the mobilisation of existing colloid sized minerals in the aquifer sediments (Ryan and Elimelech, 1996). Humic substances and layered clays may also be flushed from the soil zone during periods of high infiltration such as snowmelt or extended periods of intense rainfall (Shevenell and McCarthy, 2002). Colloid formation will not be discussed further except to say the formation and dissolution of colloids in groundwater are controlled by a large number of factors including solute concentration, redox processes (e.g. interface between oxidising and reducing groundwater), colloid surface characteristics, environmental conditions, geochemical gradients (e.g saline intrusion) and the presences or absence of other colloidal sub-particles (Buffle and Leppard, 1995a).

Once a stabilised colloid is formed in suspension within groundwater it can be transported within the groundwater system providing a mobile phase for contaminant transport, aggregated with the matrix and removed from suspension, or filtered out of suspension, (see Figure 1.2.)

It has been established, largely through laboratory-based observations, that ionic strength and chemical composition are significant in controlling the transport of colloidal suspensions e.g. (Ryan and Gschwend, 1994a; Grolimund et al., 1998), and a large amount of literature exists on colloid mobilisation and transport in model systems (Ryan and Gschwend, 1994a, b; Grolimund and Borkovec, 1999). The type of geological material can control the aqueous chemistry as well as the physical pore structure of the media and thus has a great influence on the transport of colloids.

In dual porosity systems, such as fractured or karstic aquifers, colloids may be transported very rapidly over large distances within the groundwater system (McKay et al., 2002; Shevenell and McCarthy, 2002). There has been little research on the topic of colloidal transport and mobilisation within the unsaturated zone, largely due to its structural and geochemical heterogeneity and the practical difficulties posed in establishing reliable sampling procedures (De Jonge et al., 2004b; McCarthy and McKay, 2004). A notable exception is the work of Wan and Tokunaga (1997) who introduced the concept of film straining of colloids using idealised latex particles.

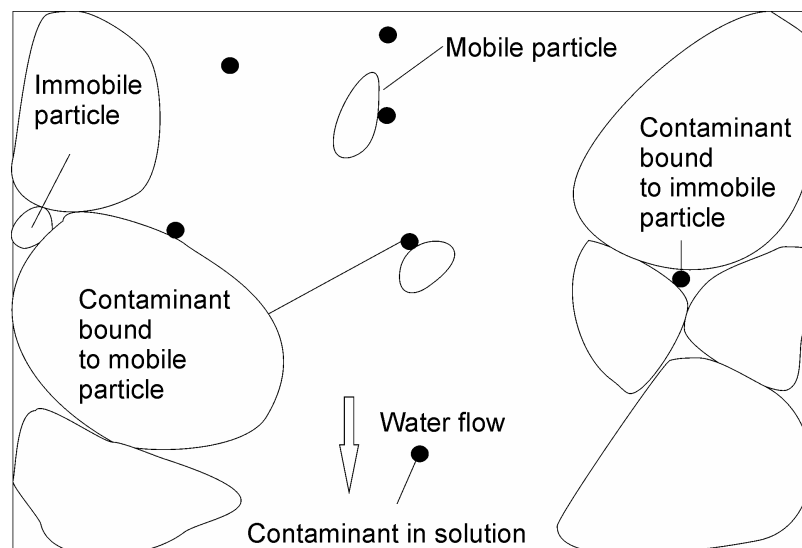
## 2 Colloid-contaminant interactions

### 2.1 COLLOIDAL PHASE TRANSPORT OF CONTAMINANTS

The extent of colloid-contaminant interaction depends intrinsically on the chemical nature of both the colloid and the contaminant as well as the physical properties of the colloidal material. Much more detailed studies have been done on these interactions within the surface water and shallow soil environment compared to the relatively deeper groundwater system.

Humic substances (humics) from soil or surface waters are able to bind hydrophobic contaminants and enhance their apparent solubility in the aqueous phase. This is also true of other biomolecules (e.g. proteins, lipids). The electrolytic surface of humics also enables binding of metal ions and charged species. Likewise, certain layered silicates clays, iron, manganese, aluminium and silicon oxides are able to bind to both inorganic metal ions and organic acids. Once bound to the colloid surface a contaminant can then be transported in the colloidal phase. Interactions are dynamic, depending on the chemical nature of the colloid and contaminant and the geochemical conditions, which means that the interactions may break down and then reform with time if for example the geochemical conditions change within a flow path.

Figure 2.1 gives a summary of colloid facilitated contaminant transport. A three-phase system is shown; contaminants in 'solution', contaminants bound to immobile particles, and contaminants bound to mobile particles. Sorption of contaminants to immobile particles, and mobile particles (colloids), may also provide sites for biodegradation of contaminants within the soil system, and to a lesser extent the aquifer system.



Source (Grolimund et al., 1996)

Figure 2.1 Colloid-facilitated contaminant transport

A wide variety of colloidal facilitated contaminant interactions, both inorganic and organic have been investigated including radionuclides (McCarthy et al., 1998), metals (Vinten et al., 1983; Grolimund et al., 1996; Karathanasis, 1999), herbicides (Piccolo et al., 1992), insecticides (Vinten et al., 1983), PAHs and PCBs (Magee et al., 1991; Marvin et al., 2004)

and bacteria (Ryan et al., 1999) to list a few. While the main focus on the research has been in surface waters and the soil system there have been a few studies that have investigated colloid contaminant interactions in groundwater systems (Backhus et al., 1993; Corapcioglu and Jiang, 1993).

## **2.2 COLLOID PHASE TRANSPORT OF PESTICIDES**

There have been a large number of studies showing the association of pesticide compounds with colloids, with soil systems as the focus for most of the work (Mustafa and Gamar, 1972; Piccolo et al., 1992; Laird et al., 1994; Seta and Karathanasis, 1997; De Jonge et al., 1998). Interaction between colloids and pesticides are predominantly first established within the soil system due to the abundance of clay minerals and organic material and the fact that this where (most) pesticides are applied. The exception to this is where the soil zone is by-passed e.g. through the use of soakaways or surface water which interacts with the groundwater system. Under such conditions pesticides may still become associated with colloidal material, either translocated from the soil zone or originating from the aquifer material.

Pesticides can be transported on colloidal material once an interaction between the pesticide and an existing colloid, or a surface that will become colloidal, has been established and provided the colloids can remain in a suspended state. Transport from the soil system to depth will be mediated by mobilisation of the colloidal material during periods of recharge. It has been shown that macroporous flow is likely to be significant in this phase of transport in sandy loam soils (De Jonge et al., 2000). Transport in the saturated zone may be through either matrix or fracture flow.

Table 2.1 gives a selection of some of the compounds that have been investigated detailing the various colloidal materials studied and the interactions/associations that have been suggested. Some researchers have investigated the nature of the association with particular colloidal fractions (Piccolo et al., 1996), and others have shown the correlation of pesticide compounds with different chemical and physical functions of colloidal material such as organic carbon and surface area (Laird et al., 1994). Research on colloid facilitated pesticide transport has often concentrated on the interactions between specific compounds with model colloidal substrates, either humic, inorganic oxides or clays (Piccolo et al., 1992; Worrall et al., 1996; Clausen and Fabricius, 2001).

Studies using soil tile drains and soil columns have shown indirect evidence for association of pesticides with colloids using indicators such as turbidity (De Jonge et al., 1998; Petersen et al., 2003) and dissolved organic carbon (Worrall et al., 1999). Studies investigating pesticides in groundwater have suggested that colloids might be significant in the transport of pesticide compounds to the saturated zone (Jorgensen and Fredericia, 1992; Gooddy et al., 2001; Gooddy et al., 2002) but very few have considered the role of colloids in pesticide transport in any detail either in the unsaturated or the saturated zone. Much more needs to be understood about the role of colloids in pesticide transport in the groundwater system in order to quantify and predict the risk of groundwater pollution from pesticides.

## **2.3 MODES AND MECHANISM OF COLLOID-PESTICIDE INTERACTIONS**

Investigations on the modes and mechanisms of interactions between humic substances with different pesticides has been possible though the use of a wide range of techniques including; infrared (IR) spectroscopy (Piccolo and Celano, 1994), fluorescence spectroscopy (Miano et al., 1992) and <sup>13</sup>C-nuclear magnetic resonance (NMR) spectroscopy (Hatcher et al., 1993).

Interactions between pesticides and humic material or inorganic colloidal material are, for the most part reversible and highly dependant on geochemical factors e.g. pH and solute chemistry, as well as other perturbations in groundwater conditions. Thus, any observations made under laboratory conditions may be useful in terms of understanding specific interactions but may not adequately represent the heterogeneity of a natural system. A summary of each of the main mechanism taken from Picollo et al. (1996) is given below:

- Ion exchange: Adsorption through cation exchange or ionic bonding operates through ionised carboxylic or phenolic hydroxyl functional groups on the humic material (HM). This only applies to a limited number of pesticides that are cationic in solution or can become so e.g. dipyridylum herbicides such as diquat and paraquat.
- Hydrogen bonding: Oxygen and hydroxyl-containing functional groups on the HM can interact with relevant groups on pesticide compound. H-bonds have been suggested between C=O groups of HM and secondary amino groups of triazines and phosphono groups on glyphosate.
- Charge transfer: Electron deficient and electron rich structures on HM (quinines and diphenols) suggest the possibility for the formation of charge transfer complexes via electron donor or electron receptor mechanism with organic molecules.
- Covalent binding: The formation of covalent bonds between pesticide compounds or metabolites and the HM mediated by enzymatic, photochemical or chemical catalysts. This form of interaction may lead to stable and irreversible incorporation with HM.

Interactions between non ionic pesticides e.g. isoproturon or atrazine and clays is greatest when the molecule is neutral or positively charged due to competition with protons, and the enthalpy of adsorption ( $\Delta H$ ) indicates that bonding takes place by physisorption (Dao and Lavy, 1978; Worrall et al., 1996).

Ionic pesticides such as bentazone or mecoprop adsorb to the surfaces of iron oxides and are strongly affected by pH and electrolyte concentration relative to non-ionic pesticides. The role of the carboxyl group in adsorption to Fe-oxides has been shown to be significant (Clausen and Fabricius, 2001). Other example of interactions with clays, HM and other organics are shown in Table 2.1.



Table 2.1 Colloid-pesticide interactions and suggested modes of association

<b>Pesticides</b>	<b>Colloidal substrate/study area</b>	<b>Suggested mode of interaction/transport</b>	<b>Reference</b>
Atrazine	HA from volcanic soil, and coal	Charge transfer complexes dominate	(Piccolo et al., 1992)
Atrazine	Clay soil	Chemisorption with coarse clay OC fraction, physical sorption with fine clay OC	(Laird et al., 1994)
Atrazine	Colloidal material fractionated from soil	Dependent on SA, CEC, OC, inversely related to clay/oxide content	(Seta and Karathanasis, 1997)
Atrazine	Soil HA and FA, coal HA and peat HA	Aromatic carbon, C=O, and COO groups	(Kulikova and Perminova, 2002)
DDT/metabolites	Shallow groundwater	Association with clay fractions	(Jorgensen and Frederecia, 1992)
Diuron	Soil adsorption and fractionation	Adsorption related to OC and SA	(Nkedi-kizza et al., 1983)
Diuron/metabolites	Small scale field soil study	Association with colloidal fraction	(Gooddy et al., 2002)
Glyphosate	HA from coal	Hydrogen bonding	(Piccolo and Celano, 1994)
Glyphosate	Comparison of sandy and loam soil	Highly sorbed, leached due to macroporous flow	(De Jonge et al., 2000)
Ioxynil	Small field scale soil study	Not sorbed, not associated with colloids	(Petersen et al., 2003)
Isoproturon	Clay and soil	Association with OC and clays	(Worrall et al., 1996, 1999)
Isoproturon	Groundwater beneath agricultural land	Association with colloidal fraction	(Gooddy et al., 2001)
Pendimethalin	Small scale field soil study	Sorbed to soil particles (turbidity)	(Petersen et al., 2003)
Prochloraz	Soil column leaching (sandy loam)	Sorbed to soil particles (turbidity)	(De Jonge et al., 1998)
MCPA, bentazone, IPU and atrazine, 2,4-D	Iron oxides; ferrihydrite and goethite	Acidic herbicides strongly sorbed, non-ionic herbicides did not sorb (atrazine/IPU)	(Clausen and Fabricius, 2001)
Thiazafluron, Metamitron	Disaggregated soil (4 clay and 1 sandy) and pure clay minerals	Associated with mineral clay fraction, not OC	(Cox et al., 1997)
Ureas, s-triazines	Isolated soil HA	Charge transfer complexes	(Senesi and Testini, 1984)

Abbreviations: HA- humic acids. FA- fulvic acids, SA- Surface area, OC-organic carbon, CEC- cation exchange capacity

### 3 Colloid-facilitated transport of pesticides to UK aquifers

#### 3.1 SOURCES, PATHWAYS AND RECEPTORS

A few studies in the UK have suggested the potential significance of colloid facilitated transport of pesticides from the soil to depth within the aquifer system (Worrall et al., 1999; Gooddy et al., 2001; Gooddy et al., 2002; Lapworth et al., 2005). This section will discuss some potential scenarios for colloid facilitated transport in UK aquifers within the framework of sources of pesticides, their pathways and likely receptors. Table 3.1 gives a summary of some of the main sources, pathways and receptors for four studies in the UK within different geological and landuse settings. It can be seen that some sources are specific to certain studies, i.e. washings from pesticide applications was considered a particularly significant source of pesticides within the context of the study by Gooddy et al. (2005), and the major source for mecoprop in the study by Williams et al. (2003) is from a landfill site. Other sources, such as pesticide spraying apply to every example but the importance of this source will vary depending on the landuse setting and agricultural practices.

Table 3.1 Suggested sources, pathways and receptors of pesticides from four studies in the UK

<b>Pesticide</b>	<b>Isoproturon</b>	<b>Mecoprop</b>	<b>Diuron</b>	<b>Mecoprop</b>
<b>Reference</b>	(Johnson et al., 2001)	(Gooddy et al., 2005)	(Lapworth et al., 2005)	(Williams et al., 2003)
<b>Aquifer</b>	Chalk aquifer of southern England	Sandstone aquifer south Yorkshire	Chalk aquifer of southeast England	Lincolnshire Limestone
<b>Sources</b>	----- Diffuse: Pesticide spraying on arable crops ----- ----- Dry deposition ----- Washings from pesticide use      Amenity/household pesticides use      Leachates from landfill waste			
<b>Pathways</b>	----- Surface runoff ----- ----- Slow matrix flow in soil and/or aquifer (limited in calcareous sediments) ----- ----- Rapid by-pass flow in soil and/or aquifer ----- ----- Potential colloidal phase transport in soil and/or aquifer ----- ----- Surface/groundwater interactions ----- ----- Drains and soakaways -----			
<b>Receptors</b>	----- Groundwater and surface waters -----			

In each of the above examples there will be large differences both in terms of physical factors; geochemical environment, seasonal recharge, antecedent conditions and anthropogenic factors; agricultural practice and landuse which will vary greatly both within and between study sites.

The following section discusses three hypothetical examples from the UK, highlighting the importance of different sources, pathways and receptors on transport of colloidal bound pesticides to aquifers.

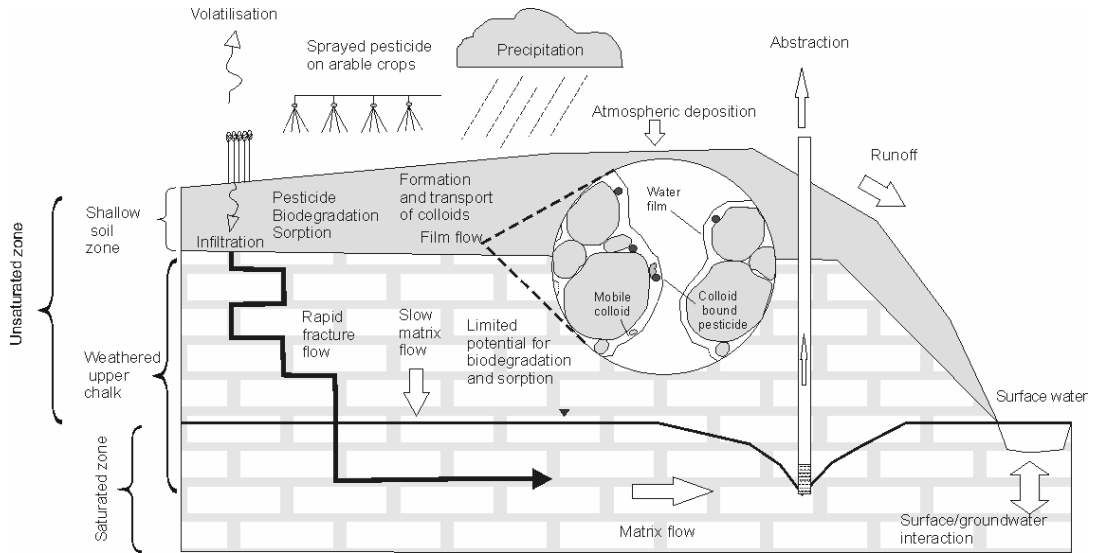


Figure 3.1 Schematic representation of diffuse source colloid facilitated pesticide transport

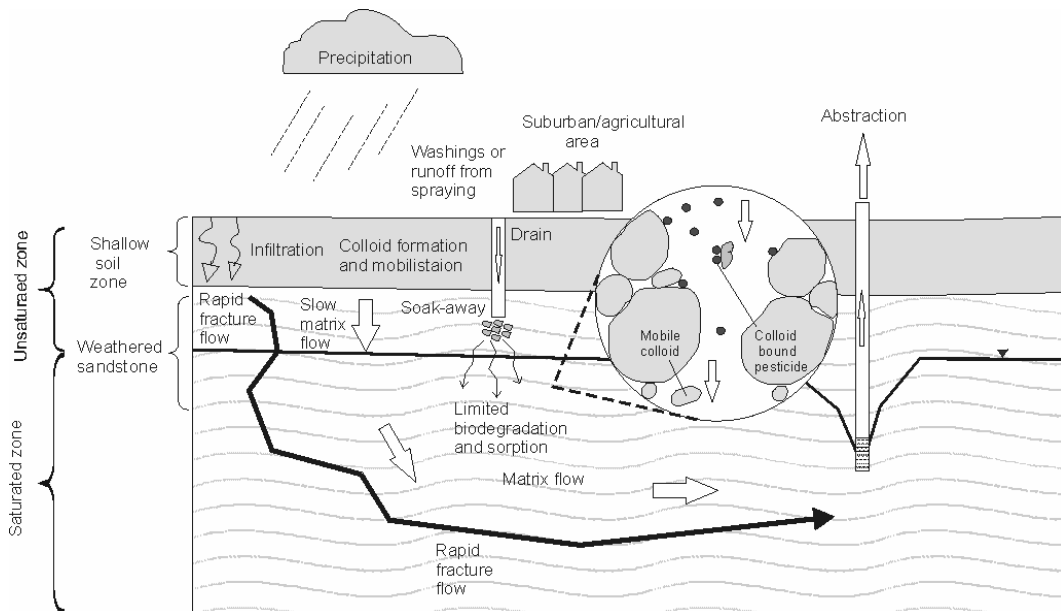


Figure 3.2 Schematic representation of point source colloid facilitated pesticide transport

Figure 3.1 shows a schematic representation of diffuse pesticide sources from arable agriculture on the upper chalk, somewhat analogous with the example from south England in Table 3.1, and the role of colloid formation and interaction with pesticides within the soil

zone. Once the colloid-pesticide phase is stable it can move through the relatively thin soil zone either by rapid by-pass flow or film flow some retardation of this film flow is likely to occur due to film straining as the soil matrix dries out. Matrix flow is less likely given the small pore sizes (0.5-1 $\mu$ m)(Price et al., 2000). It is in the soil zone that there is the greatest potential for biodegradation and sorption to humic substances and other colloidal matter.

The thick unsaturated zone of the chalk allows greater potential for diffusive exchange and dilution during transport, but fractures in the weathered chalk matrix do allow rapid routes to the saturated zone. There is relatively little potential for biodegradation within unsaturated chalk matrix. Runoff will also transport colloid bound pesticides from the soil zone to reach surface water. This may also provide a pathway to the groundwater system if there is hydraulic continuity between the groundwater and surface water. This may be an important pathway in low-lying agricultural areas such as parts of Norfolk and southeast Yorkshire which have shallow unsaturated zones and are drained by dykes and canals.

Figure 3.2 show a schematic representation of colloid facilitated transport of pesticides from point sources overlying a sandstone aquifer with a shallow unsaturated zone. In this scenario colloids are formed and transported from the soil zone and aquifer, and the source of pesticides is from drains and soak-aways that by-pass the soil zone. Colloid-pesticide interactions are only possible within the lower unsaturated zone and saturated zone. Pesticide concentrations may be much higher than would be expected as a result of transport from agricultural/amenity applications on the soil surface as the potential for sorption and biodegradation is much reduced. Once stable in the colloidal phase pesticides can be transported further and faster than would be predicted from dissolved solute transport, as the process of diffusion is limited due to the size of the colloidal particles.

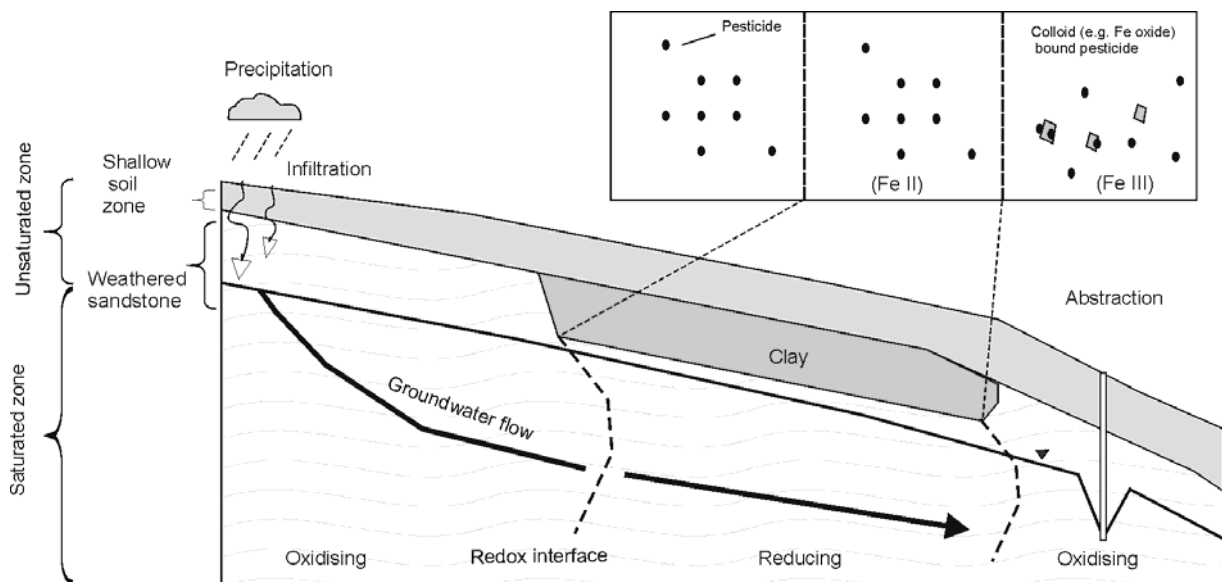


Figure 3.3 Colloid formation and enhanced pesticide transport at the redox interface

Figure 3.3 shows a schematic representation of the anoxic/oxic interface within a sandstone aquifer. Oxidising groundwater (including pesticides) may travel into relatively reducing conditions, where Fe is in the reduced form as dissolved  $Fe^{2+}$ , for example beneath a clay aquitard. As groundwater moves across the interface into the oxidising conditions down the

flow path there is an increased potential for colloid formation (e.g. Fe oxide) as well as the potential for certain acidic pesticides (e.g. mecoprop or bentazone) to associate with this colloidal phase. Due to the formation of colloids at the redox interface and following the formation of colloidal-pesticide interactions the pesticides could be transported faster and further than might be predicted by solute transport alone, for reasons previously discussed, and provide a rapid mechanism for pesticide transport to the abstraction borehole.

## 4 Sampling groundwater colloids

The way in which a groundwater sample is collected may effect the amount/type of colloidal material found in the sample (Backhus et al., 1993). For a sample to be ‘representative’ of the colloids in suspension under natural groundwater flow it is important to not introduce colloids into the groundwater system as an artefact of the sampling method, or filter colloids out by pumping too fast relative to groundwater velocity.

Colloids can be introduced as a result of the borehole construction process (e.g. drilling mud), and pumping may shear otherwise immobile colloids from localised aquifer sediments (Ryan and Gschwend, 1990). This does depend to a large extent on the maturity and design of the borehole. A borehole that is well developed and has been in operation for a long time will not be necessarily prone to the same problems of artificially-induced colloidal material during pumping, as the most easily accessible material would already have been removed from the capture zone of the borehole. Colloids may also be generated in-situ due to changes in geochemical conditions. The issue of obtaining a representative sample is complicated further if seasonal variations in colloidal fluxes are considered.

The geochemistry of the groundwater system needs to be maintained, this is especially important in aquifers with reducing conditions; Ryan and Gschwend (1990) recommend that groundwater needs to be pumped at a low flow rate (~100 mL). As in the case of any bulk groundwater sample the borehole needs to be purged sufficiently to remove the standing water in the borehole.

It is important that the sample is collected in a way that will not compromise the contaminant of interest either by sorption to sampling material or loss due to volatilisation. Samples need to be stored under suitable conditions that will not lead to loss of contaminants or will change the nature of the colloidal material in the sample.

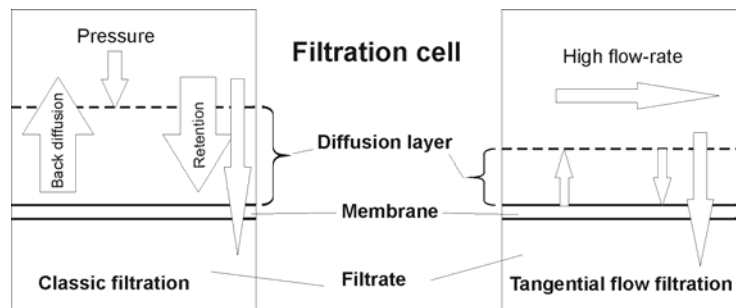
### 4.1 FRACTIONATION OF COLLOIDAL MATERIAL

The suspended colloidal material can be separated from the dissolved aqueous fraction principally in two ways, filtration and centrifugation. Some studies have used a combination of the two to investigate colloidal particles (McDowell and Sharpley, 2001). Conventional filtration methods such as operationally defined 0.45 $\mu\text{m}$  filters have been used for environmental studies to separate the dissolved and solid fractions, however colloidal particles span a wide range of pore sizes and are therefore difficult to study using these methods (see Figure 1.1). Ultrafiltration (using high pressure) has been used to fractionate samples, but this method is plagued with the problem of concentration polarisation effects and membrane clogging due to colloid aggregation on the surface of the membrane (Heathwaite et al., 2005). This is a particular problem for reducing samples with high concentrations of  $\text{Fe}^{2+}$ .

The use of Tangential-Flow Fractionation (TFF) has been investigated as a better method for fractionation (Grueguen et al., 2002; Morrison and Benoit, 2004), as the tangential arrangement minimises the clogging at the membrane surface. Although this is an improvement on the classical method of filtration it does not avoid coagulation altogether. Figure 4.1 gives a schematic representation of filtration using classic pressure filtration and tangential flow filtration.

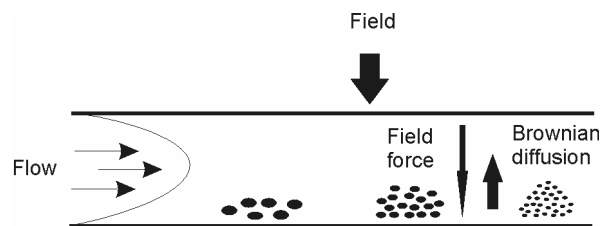
Field-Flow Fractionation (FFF) (see Figure 4.2) has been developed with some success as a method for colloid separation (Buffle and Leppard, 1995b). This method uses the physical

properties of the colloids and applies both a horizontal flow and a field perpendicular to this flow to the injected sample allowing the different sized colloids to accumulate. A chromatographic type elution profile of the different colloid sizes is obtained once the sample is allowed to flow out of the system. For environmental applications sedimentation FFF, where the channel is placed in a centrifuge and the force of gravity is used, and flow FFF, where a cross-flow is applied to the stream, have been the most useful systems. One drawback of the FFF system is that the colloids are significantly diluted during the process compared to the injected colloidal material.



Source:(Buffle and Leppard, 1995b)

Figure 4.1 Classic filtration and tangential flow filtration



Source:(Buffle and Leppard, 1995b)

Figure 4.2 Field-Flow-Fractionation

## 4.2 HANDLING AND STORAGE OF GROUNDWATERS

It is important to minimise processes that will eliminate colloidal material from the sample, or in the case of reducing waters lead to the formation of colloids. Overall change within the system should be slowed as much as possible to preserve a sample that is as close to the groundwater conditions as is practically possible. Below is a list of factors that should be considered when handling and storing a groundwater:

- Minimise adsorption to vessel walls by preequilibration and the use of inert vessels (e.g. glass or stainless steel)

- Reduce microbial growth and degradation of organics by minimising contamination during sampling, by refrigeration and restricting contact with light
- Minimise aggregation of small colloids by flotation at the air-water interface. Changes in temperature can lead to the formation of micro-bubbles which catalyse the formation of such aggregates
- Minimise contact with O<sub>2</sub> as this changes in groundwater chemistry, this is critical for reducing waters which may lead to the formation of iron oxides
- Avoid prolonged agitation of sample as this will lead to desegregation of colloidal fractions

### 4.3 GROUNDWATER FRACTIONATION BY TANGENTIAL AND CLASSICAL FILTRATION METHODS TO INVESTIGATE PESTICIDE TRANSPORT IN UK

Figure 3.4 shows an example of how the TFF techniques might be used to investigate colloidal phase pesticide transport in groundwater. Some suggestions are made on how to sample and characterise the groundwater. Prior to pesticide analysis by HPLC pre-concentration of the sample is carried out using solid phase extraction. Given the pre-concentration step (~x2000), and associated matrix effects, it is essential that the pesticides of interest are present in the sample at concentrations >0.01µg/L.

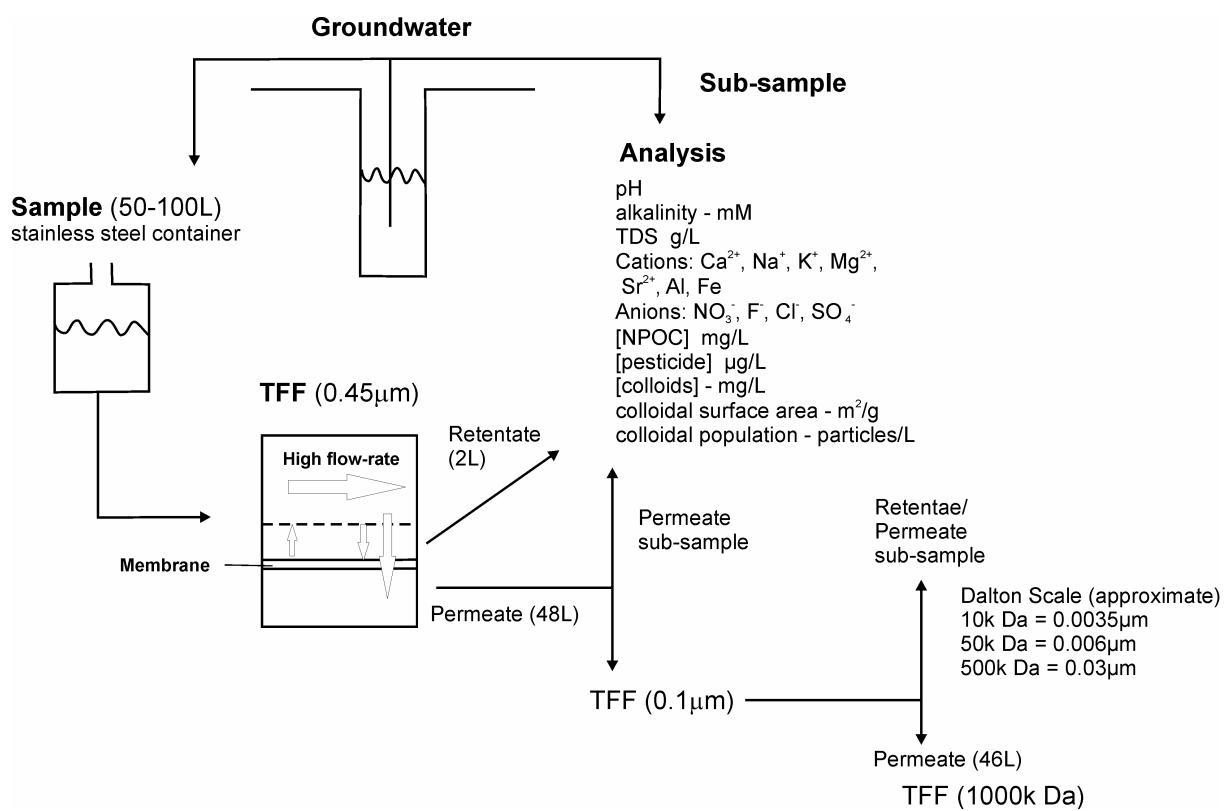


Figure 4.3 Tangential flow fractionation of groundwater for colloidal phase transport of pesticides



Groundwater samples might also be fractionated using classical filtration methods, although this system may be problematic if there is a very high colloidal load in the sample. This was done in the field using a sterile container that could be pressurised by hand (<20psi). Figure 4.4 shows a schematic of equipment that can be used. This method is useful for investigating anaerobic waters as changes in groundwater chemistry are minimised in the sealed container, and the filtration step is completed very quickly. The filters can also be retained and stored for later analysis of the solid phase on the surface of the membrane.

Fractionated groundwater samples need to be collected in appropriate containers e.g. brown glass bottles with airtight caps, it is also essential that the containers are filled to the top to exclude any air from the sample during the storage and transportation phase. Samples should be transported in a cool box to maintain groundwater temperature and stored in a refrigerator at ~5°C prior to solid phase extraction and analysis by HPLC for pesticides.

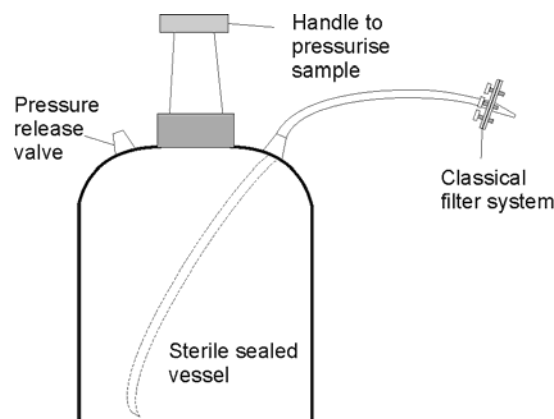


Figure 4.4 Classical filter system for fractionation of groundwater in the field

Using TFF and classical filtration to fractionate groundwater samples from anaerobic aquifers has additional challenges due to the formation of Fe oxides on contact with air. The use of an anaerobic 'glove-box' to fractionate the samples could be used to preserve a sample that is as close to the groundwater conditions as is practically possible.

## 5 Conclusions

A large amount of literature exists on colloid facilitated transport of pesticides, but the majority of this work has laboratory-based studies focussed on the soil zone using isolated humic materials or using idealised colloidal systems, e.g. latex. Some recent studies have investigated the transport of colloids in the unsaturated zone, however the issues of heterogeneity and complexities of recharge events are challenges that need further investigation.

Colloid facilitated transport of pesticides in groundwater has been suggested as potentially significant transport mechanism but very few studies have addressed the issue in any detail within a natural aquifer system. While many studies have looked at the interactions between metals/metalloids and colloids in groundwater systems, much less work has been done on interactions of organic contaminants with colloids.

Colloids are ubiquitous in the subsurface environment, and may increase the mobility of pesticides from the point of application to groundwater. TFF, FFF and to a limited extent classical filtration coupled with HPLC show potential as techniques for investigation pesticide-colloid interactions within UK aquifers. The challenge of using these methods to investigate anaerobic groundwaters does need to be addressed to further the understanding of colloid facilitated pesticide transport in groundwater systems.

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