

The significance of colloids in the transport of pesticides through Chalk

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Abstract

Agrochemical contamination in groundwater poses a significant long term threat to water quality and is of concern for legislators, water utilities and consumers alike. In the dual porosity, dual permeability aquifers such as the Chalk aquifer, movement of pesticides and their metabolites through the unsaturated zone to groundwater is generally considered to be through one of two pathways; a rapid by-pass flow and a slower 'piston-flow' route via the rock matrix. However, the dissolved form or 'colloidal species' in which pesticides move within the water body is poorly understood. Following heavy rainfall, very high peaks in pesticide concentration have been observed in shallow Chalk aquifers. These concentrations might be well explained by colloidal transport of pesticides. We have sampled a Chalk groundwater beneath a deep (30 m) unsaturated zone known to be contaminated with the pesticide diuron. Using a tangential flow filtration technique we have produced colloidal fractions from 0.45 μ m to 1kDa. In addition, we have applied agricultural grade diuron to a typical chalk soil and created a soil water suspension which was also subsequently fractionated using the same filtration system. The deep groundwater sample showed no evidence of association between colloidal material and pesticide concentration. In comparison, despite some evidence of particle trapping or sorption to the filters, the soil water clearly showed an association between the <0.45 μ m and <0.1 μ m colloidal fractions which displayed significantly higher pesticide concentrations than the unfiltered sample. Degradation products were also observed and found to behave in a similar manner to the parent compound. Although relatively large colloids can be generated in the Chalk soil zone,

it appears transport to depth in a colloidal-bound form does not occur. Comparison with other field and monitoring studies suggests that rapid by-pass flow is unlikely to occur beneath 4-5 m. Therefore, shallow groundwaters are most at risk from rapid transport of high concentrations of pesticide-colloidal complexes. The presence of a deep unsaturated zone will mean that most of the colloidal-complexes will be filtered by the narrow chalk pores and the majority of pesticide transport will occur in a 'dissolved' form through the more gradual 'piston-flow' route.

Introduction

Agrochemical contamination of groundwater has been identified as an increasing problem in Europe (Skark and Zullei-Seibert, 1995) and the UK (Environment Agency, 2002). Recently the occurrence of both pesticides and their metabolites within groundwater have been identified (Kolpin et al., 1996, 2004; Gooddy et al., 2002, 2005; Johnson et al., 2001; Postle et al., 2004). Pesticides in groundwater have been found to originate from arable land (e.g. Gooddy et al., 2001) as well as a number of non-agricultural sources, such as landfills (Harrison et al., 1998), railway lines (Schweinsberg et al., 1999) and amenity use (Lapworth and Gooddy, 2006). A recent study looking into the impact of climate on pesticide behaviour in the environment (Bloomfield et al., 2006) has suggested the types of pesticide and rates of application are likely to be altered to reflect significantly modified rainfall seasonality and intensity as well as increased temperatures resulting in likely changes in land-use. Therefore a process based understanding of pesticide transport must be seen as a priority in the protection and maintenance of potable water resources

Along with the dynamic of water flow, pesticide transport from the soil surface to groundwater is controlled by several process including plant uptake, sorption to solid phases, microbially mediated degradation and 'dissolved' and colloidal phase migration (Foster et al., 1991; Chilton et al., 2005). Colloids have been operationally defined as particles with diameters less than 10^{-5} m (10 μ m) (Stumm, 1977). Colloids are often generated in the soil system by dispersion from soil aggregates in response to rainfall and infiltration (Ryan and Elimelech, 1996). Colloids in the subsurface can significantly enhance the mobility and transport of contaminants (McCarthy and Zachara, 1989) especially those that are comparatively insoluble (Grolimund et al., 1996). Studies suggest that colloids are able to move through porous media even when the degree of saturation is very low (Harvey and

Garabedian, 1991; Wan and Tokunaga, 1997). Numerous studies have been undertaken that show pesticide can sorb to colloids and potentially enhance their transport (e.g. Vinten et al., 1983; Worrall et al., 1999; Seta and Karathanasis, 1997; Kulikova and Perminova, 2002).

The Chalk, the major UK aquifer, is a soft microporous and fractured calcium carbonate aquifer with dual porosity and dual permeability. It is an extremely important resource providing 15% of the water supply nationally and up to 35% regionally in the south and east of England and is under increasing stress from increased rates of abstraction and from contaminant sources. Flow through the Chalk unsaturated zone is often believed to be by a combination of two main mechanisms; intergranular seepage through the matrix, sometimes termed 'piston flow' (e.g. Price et al 1976; Price, 1993); and rapid movement through fractures (e.g. Headworth, 1972), often referred to as 'preferential flow'. The Chalk matrix is a very fine grained porous media with median pore-throat sizes of the order of 0.1 μ m (Price, 1976). This is narrow and provides a degree of natural filtration of an infiltrating recharge water. Indeed, colloidal particles larger than 0.1 μ m are unlikely to pass through the matrix and might therefore be more likely to penetrate the chalk through a preferential flow path.

Shand and Bloomfield (1995) found evidence for the transport of soil particles down to 3m along fracture surfaces in the chalk. Iron-rich clays were found to be prominent at shallow depths. In a study by Goody et al. (2001), high concentrations of the herbicide isoproturon were found in shallow chalk groundwater (3-5 m) by using a static sampler system that collected recent recharge water arriving at the water table. As concentrations of isoproturon increased there was no concomitant rise in nitrate. Although no direct field measurements were made, the workers hypothesized that the isoproturon had moved through the soil and unsaturated zone by a preferential flow route sorbed to soil colloids. A related study by Johnson et al. (2001) found even more compelling evidence for colloidal transport of pesticides. In this study high concentrations of the herbicide isoproturon were found in pumped shallow Chalk groundwater following intensive rainfall events for three successive years after the herbicide was last applied. Both of these herbicide studies strongly suggested a colloidal source of pesticides in the shallow groundwater as concentrations of non-sorbing solutes such as agriculturally derived nitrate and chloride did not show the same relationship with rainfall intensity and soil particles acted as a long term source of the contaminant.

Suspended colloidal material can be separated from the dissolved aqueous fraction principally in two ways, filtration and centrifugation. Conventional filtration methods such as operationally defined 0.45 μ m filters have been used for countless 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. 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). The use of Tangential Flow Fractionation (TFF, also called cross-flow filtration) has been investigated as a better method for fractionation as the tangential arrangement minimises the clogging at membrane surfaces (Morrison and Benoit, 2004). Although this is an improvement on classical methods of filtration it does not avoid coagulation altogether. Most systems also generally require a relatively large sample volume (i.e. >100 mL) which can be a constraint to some experimental procedures.

Tangential-Flow Fractionation has grown in popularity as the fractionation technique to use in the field of water research. Li et al. (2004) characterised humic acids which had previously been fractionated by TFF. Guéguen et al. (2002) have used this technique to demonstrate that TFF can produce reliable fractionations of natural organic colloids in aquatic systems. Olivie-Lauquet et al. (2000) have used TFF to characterise groundwaters and surface waters for both organic and inorganic colloidal material. Other workers have also recently demonstrated this technique to be effective in groundwater systems (Hassellöv et al., 2007).

In this study we have used tangential flow filtration to fractionate natural colloidal material from soil and groundwater. We have examined the colloid-pesticide association in calcareous soil suspensions where the pre-emergent herbicide, diuron (3,4-dichlorophenyldimethylurea), has been recently applied, and in a sample of relatively deep chalk groundwater known to be contaminated with diuron. The objectives of this study are to determine whether pesticides (and their degradation products) can form stable complexes with colloidal material present in the soil zone, and if these complexes also exist in groundwater beneath a relatively deep unsaturated zone. By considering our findings in relation to recently published field studies (Haria et al., 2003; Ireson et al., 2006) and modelling investigations (Mathias et al., 2005; Mathias et al., 2006), we present two conceptual models for pesticide movement from the point of agricultural application to the groundwater beneath.

Materials and Methods

Soil Sampling

Chalk soil samples (roughly 50 kg) from southern England were taken from the top 15cm of an agricultural soil profile using an auger. Root material and any residual crop from within the root zone (approximately the top 5cm) was discarded, as was any gravel-sized material. The soil was homogenised and a subsample of 20 kg spread out over area of 1m², with an approximate depth of 1cm. 1000mg of KarmaxTM (Dupont agricultural grade diuron) with a 83% diuron content was dispersed in 2000mL of ultra-pure water and irrigated evenly over the soil sample and left to soak into the soil for two hours. This gave an equivalent loading of 6.7 kg/ha, the same as previously used in a field based degradation trial by Gooddy et al (2002). Duplicate soil suspensions with solid solution ratios of 1:5 were prepared using 2.4kg of the irrigated soil (equivalent to 41.5mg diuron) and 12L of ultrapure water. The mixtures were agitated for 30 minutes and then allowed to settle. One sample was allowed to settle for 10 hours prior to decanting 10L of the supernatant into brown glass bottles. The suspensions were stored in the dark at approximately 20°C to allow microbial degradation of the diuron to take place. The other sample was agitated periodically, settled and decanted after 63 days. The decanted samples were stored at 3°C prior to analysis and fractionation using tangential flow fractionation.

Groundwater Sampling

A site in southeast England where a previous diuron contamination had been reported (Lapworth and Gooddy, 2006: site 14) was chosen for the groundwater sample. The borehole sampled is cased down to approximately 10 m with the water table at 31 m at the time of sampling. The total depth of the borehole is 36 m. The borehole was purged prior to sampling to obtain a fresh raw groundwater sample. The sample was taken directly from a stainless steel sampling tap on the rising-main of the borehole. Appropriate protocols were followed to minimise the risk of artificially creating or mobilising colloids during sampling (Backhus et al., 1993). Two sterile 50L stainless steel sample containers, (Ucon Containersysteme AG, Germany) with stainless steel plugs and PTFE seals, were used to collect and store the groundwater. The samples were placed in a cold store and stored in the dark at 3°C within 3hours of taking the sample to minimise microbiological activity.

Tangential Flow Filtration

For any given tangential flow system two fractions are usually generated. The ‘permeate’ fraction is that which passes through the TFF membrane, whereas the “retentate” is that which is retained by the ultrafiltration membrane. The latter is enriched with colloids, which have not passed through the membrane. To concentrate colloidal material, water from the sample reservoir is pumped across the ultrafiltration membrane from where the permeate is isolated in a separate reservoir whilst the retentate is recycled back into the sample reservoir. The concentration of colloids increases with time. A schematic diagram of the system is shown in Figure 1.

Tangential flow filtration was carried out on all samples by using a Pelicon 2 ultrafiltration unit (Millipore, UK). The whole system comprises a peristaltic pump, an acrylic holder and an ultrafiltration cassette. Six cassettes were used in series and in decreasing size. For the smaller sizes the filter cassettes are differentiated in terms of kiloDaltons (kDa) since fractionation at this scale is carried out on a molecular mass basis. The cassettes used were 0.45 μ m, 0.1 μ m, 1000 kDa, 100 kDa, 10 kDa and 1k Da respectively. These are all made of regenerated cellulose and have a surface areas of 0.50m². Cleaning of the filters was carried out in accordance with the procedure used by Guéguen at al. (2002).

For the chalk/soil suspension samples a flow rate of 37 mL/min for the permeate was maintained. This flow rate allowed for reasonable sample processing times without generating excessively high pressures which might cause tubing to malfunction or split. Permeate volumes for these samples started at about 5L for the 0.45 μ m filter. For the groundwater sample due to the lower colloidal content the permeate flow rate was increased to 50 mL/min and a larger initial permeate volume of 75 L was used. Generally the processing of 5L took between 2-2½ hours.

Diuron and Metabolite Analysis

Analysis of diuron and its principal metabolites was accomplished by reversed-phase HPLC separation employing isocratic elution in conjunction with UV detection of the separated components. The method used is similar to that previously published by Field et al. (1997) and as modified in Goody et al. (2002) . For the soil suspension samples the limit of

detection was *ca.* 0.002 mg/L. For the groundwater samples it was necessary to initially pre-concentrate the samples by C18 SPE cartridges (Waters Oasis HLB 60mg). Against standard solutions for phenylureas this process gave a 96% recovery for diuron, 93% for primary degradation product dichlorophenylmethyl urea (DCPMU), 96% for the secondary degradation product dichlorophenyl urea (DCPU) and 83% for the tertiary degradation dichloroaniline (DCA). The limit of detection was *ca.* 0.005 µg/L.

Results

Soil Pesticide-Colloid complexes

Pesticide analysis of the raw soil water suspension and subsequent fractions obtained by tangential flow filtration from the initial sample (i.e. 12 hours after application) are shown in Figure 2. Data is shown for both the parent compound and any degradation products found. The tangential flow fractions are shown in two parts; the retentate, corresponding to material which would not pass through a filter of this size, and the permeate, which corresponds to material which is small enough to get through the filtration mesh. In all cases the concentration in the retentate exceeds that of the permeate, but it is only in the case of the >0.45µm and >0.1µm retentate fractions that the concentration exceeds that found in the unfiltered water.

The distribution of the relative fractions and the resulting pesticide and metabolite concentrations observed after 63 days are shown in Figure 3. Of note is the appearance of two additional degradation products, DCPU and DCA. However, compared with previous soil degradation studies carried out by Goody et al (2002), the concentrations of the degradation products relative to the parent compound are low. In a similar manner to the original sample, concentrations of diuron only exceed the unfiltered water concentration in the >0.45µm and >0.1µm fractions of the retentate. The same is also true for DCPMU, whereas the retentate concentration of DCPU only exceeds the unfiltered water concentration in the 0.45µm fraction. This may reflect the limits of detection of the method rather than indicate anything more significant about the degree of pesticide binding. The same is likely to be true of the DCA pesticide data. It is interesting to note that the ratios between the retentate and the permeate are remarkably similar between the two samples which gives a significant degree of credibility to the method used (see tables 1 and 2).

Tables 1 and 2 show the mass balance through the filtration experiment, by multiplying the detected concentration of diuron by the volume of water in either the permeate or retentate (the degradation products have been omitted from this calculation since the contribution to the overall mass balance is small, typically contributing <1% of the total pesticide mass). In both cases it is revealed that a significant mass of diuron is lost during the experiment. Interestingly, the relative mass losses between the two samples are nearly identical which suggests that the same phenomena is responsible for the pesticide removal. One possible cause of this concentration reduction is sorption to the filters which is contrary to the findings of Guéguen et al. (2002) and Hoffman et al. (2000) who found good recovery for DOC and NOM respectively using the same regenerated cellulose filters. Indeed, studies we have carried out have also shown good recovery for DOC, with the majority concentrated in the 1kDa fraction, indicative of fulvic acids (Gooddy et al., 2006). However, evidence of sorption of some pharmaceutical chemicals to regenerated cellulose-based membranes has been reported by Burba et al. (2005). Significantly the nominal surface area of all the ultrafiltration cassettes is 0.5 m² but the rate of removal is not constant so sorption may not be the only process causing the observed concentration drop. Alternatively, the colloidal material may be getting entrapped in the filter matrix, however, blank procedures ran between fractions showed no desorption or disentrainment of any pesticide material. Another possibility for the mass loss could be due to coagulation and flocculation of colloidal material as a result of the change in concentration of charged ions in the permeate solution. This can lead to the formation of an insoluble precipitate that would not be captured in the HPLC analysis and so ostensibly lost from the mass balance calculations.

Although this is an important observation in terms of the overall TFF method for fractionating pesticides, it is considered that the overall finding of greater association with the larger colloidal fraction is still valid and of significance in terms of pesticide transport. Additionally it should be noted that the concentration of the pesticide in the 0.45µm and 0.1µm retentates is much greater than the mass of pesticide lost from these two fractions.

Groundwater Pesticide Colloid Complexes

Three of the phenylurea concentrations (DCPU has been omitted for clarity but follows a very similar pattern to DCPMU) for the unfiltered water and 6 retentate fractions taken from the groundwater sample are shown in Figure 4. The parent compound, diuron shows a decrease of

roughly 20% in concentration from 2.3 µg/L in the raw water to roughly 1.8µg/L in the 0.45µm fraction. The subsequent four fractions remain at this relatively constant concentration before a further slight decrease in concentration in the 1kDa retentate. DCPMU shows a more rapid decrease in concentration between the raw water and the 0.1µm retentate (nearly 60%) before stabilising at this concentration. DCA shows very rapid initial decline in concentration from 2.8 µg/L in the raw water to 1.5 µg/L in the 0.45µm retentate. These concentrations remain stable until declining again in the final two fractions. There is no evidence for any colloidal-pesticide complexes existing in this sample.

The relatively high concentration of degradation products and the decline in concentrations of all the phenyl urea compounds may be indicative of some degradation occurring during the experiment since relatively large volumes of water were being processed which require at least 24 hours per retentate fraction. However, this rate of removal is considerably in excess of degradation rates observed (Gooddy et al., 2002) where 20% of the parent compound had been converted to metabolites in the soil matrix after 50 days and it is unlikely to be the primary reason for the loss in concentration during the experiment. Some sorption or entrapment on to the filtration cartridges along with the formation of insoluble precipitates in the permeate are therefore again suspected. Even with these losses it appears that there is no relationship between colloidal fraction and pesticide for a groundwater sampled from roughly 30 metres below ground level.

Discussion

These experiments have demonstrated that pesticides will form an association with colloids from a calcareous soil and produce pesticide-colloid complexes which have a size generally in excess of 0.1µm. However, in a groundwater sample taken from depth no such association with colloids is observed. This is despite the previous observations of Johnson et al. (2001) and Gooddy et al (2001) which strongly suggested that pesticide concentrations in the shallow groundwater were controlled, at least in part, by the association of pesticides with colloidal material. This infers that either our method was too insensitive analytically to detect pesticides bound to colloids in the groundwater, or that the pesticide present was in a free (i.e. unbound) form and that the colloidal material had been removed during the migration of the water through the unsaturated and/or saturated zone prior to sampling.

If we consider the first case, and assume that our analytical method is too insensitive, some simple calculations can be performed to confirm or refute this.

Assuming an initial total volume of groundwater of 50 litres, and a retentate volume of 900 ml, this would produce a colloid pre-concentration factor of 55.6 (the ratio of the initial volume to the retentate volume). With an initial pesticide concentration of $4\mu\text{g/L}$ and an assumed pesticide-colloid association percentage of, for example 5%, after one full filtration cycle the permeate would have a pesticide concentration of $3.8\mu\text{g/L}$ and the retentate would have a pesticide concentration of $14.9\mu\text{g/L}$. We can repeat this for a range of association percentages as demonstrated in Figure 5 where the % of pesticide-colloid associated compounds ranges from 5% down to 0.1%.

An initial concentration $2.3\mu\text{g/L}$ has been used for diuron and an analytical error of $\pm 5\%$ has been assumed to reflect the conditions observed in the groundwater fractionation. The graph demonstrates how the difference between the retentate increases as the percentage of pesticides associated with colloids increases. The graph also demonstrates that there is clear divergence between the retentate and permeate concentrations where just 0.3% of the pesticide is associated with colloidal material, even with the analytical variation of $\pm 5\%$. The data presented in Table 1 and 2 for the $>0.45\ \mu\text{m}$ and $>0.1\mu\text{m}$ retentate fractions both have colloid-pesticide association factors close to 3.5%. Therefore, the method appears to be sensitive enough to detect even a small degree of pesticide-colloid association. Hence, we suggest that colloidal material and the pesticides associated with it have been removed somewhere between the soil zone and the saturated zone from where the sample was taken.

Previously there has been much evidence cited to support the existence of significant bypass flow in the Chalk. This includes the observed rapid response of the water table after high intensity rainfall events (Headworth, 1972) and the appearance of bacteria in abstraction waters (Maclean, 1969). By contrast, a study by Smith et al. (1970) examining the tritium content in unsaturated zone pore-waters led to the suggestion that flow through the Chalk unsaturated zone was predominately through the matrix at a mean rate of around 0.8 m/year. A generation of models got round this by assuming flow to occur exclusively in fractures with solute transport being retarded by molecular diffusion into the matrix (Oakes et al., 1981; Barker and Foster, 1981). However, through using a transient flow and transport, dual-permeability model and examining the effects of diffusion in the Chalk unsaturated zone,

Mathias et al. (2005, 2006) showed that, at depth, almost all of the flow in the unsaturated zone was in the matrix.

In the very shallow unsaturated zone, just below the soil layer, Ireson et al. (2006) found that at 0.4 and 1.0 m depth there tends to be a rapid increase in matric potential straight after the main rainfall events, which was followed by a more gradual recession, as the profile drained. However, below 4 m depth this was completely attenuated and only a long-term rise was noticed. A similar feature can also be seen in the matric potential data presented by Hodnett and Bell (1990). These higher matric potentials allow more of the fractures to hold and transmit water, as was found by Haria et al. (2003). Consequently preferential flow can occur in fractures in the top 4-5 m of the Chalk unsaturated zone, but it is unlikely to occur at greater depths.

It would appear therefore that the previous observations of Gooddy et al (2001) and Johnson et al (2001) pertaining to the likelihood colloidal transport of pesticides were correct. The fact that they were found at the study site was a function of the shallow depth from which the samples were taken. Preferential flow of colloiddally associated pesticides was able to occur down to sufficient depth to allow the large particles to reach the water table without being filtered out by the small pore-throat size of the Chalk matrix.

We can therefore propose two conceptual models for pesticide transport to chalk groundwater; one where the unsaturated zone is shallow and colloiddally mediated transport of pesticides can be deemed a important and rapid (Figure 6a), and the other where the unsaturated zone is deep and the majority of the colloiddal material which has been identified by this study to form pesticides complexes (i.e. particles $>0.1\mu\text{m}$) is removed by the narrow apertures of the chalk matrix (Figure 6b). In both of these models it is worthy to note that pesticides can also move in the 'dissolved' phase through both the matrix and the fractures. However, the important aspect of the colloiddally bound route is that poorly soluble compounds (like most pesticides which would be expected to reside in the soil at the point of application) are made considerably more mobile and there is the potential for relatively high concentrations of pesticides to enter the shallow groundwater system.

Conclusions

Through this study we have found that the calcareous soils, typical of those overlying the Chalk aquifer in most of southern England, can form pesticide-colloid complexes. These complexes contain particles that are mostly larger than 0.1 μ m. Metabolites, which are subtly different in structure, behave in an analogous manner to the parent compound which suggest the binding mechanism is the same between the different molecule types. There is evidence for some sorption or entrapment of diuron (and metabolites) to the regenerated cellulose filters and the possibility that some precipitates have been formed during the filtration process..

No association was found between colloids and pesticides in the deep groundwater. Based on data from previous studies we have interpreted this finding in terms on the relative importance of the properties of the chalk unsaturated zone as a effective barrier to colloid-pesticide complexes. Shallow groundwaters are therefore more vulnerable to contamination not just because the potential travel distance is shorter but because they allow colloidally-complexed pesticides (and by inference, other organic contaminants) to reach the water table by a rapid route. Compounds that are relatively insoluble and considered immobile may therefore enter a groundwater body. The presence of a deep unsaturated zone will mean that, because of their size, most of the colloidal-complexes will be removed by filtration as they pass into the narrow chalk pore-throats. In this case the majority of pesticide transport will occur in a 'dissolved' form through the more gradual 'piston-flow' route.

In terms of practical considerations of this finding, it may be important for land-use management and manure applications where the depth to water is shallow. On Chalk down-land this may mean not applying agricultural wastes in the lower parts of the valley, even where no surface water body is evident or close-by. Additionally it implies that deeper groundwaters are relatively well protected from sudden pulses of pesticide contamination following application or a spill. The filtration of pesticides bound to colloids will also decrease the net loading to groundwater. Producing pesticides that are strongly bound to soil colloids, and remain bound, may therefore act as a good groundwater protection measure.

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