

The Behaviour of Atrazine and Simazine within the Chalk Aquifer

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National Rivers Authority

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Experimental Results and Interpretation

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EXECUTIVE SUMMARY

The results obtained reveal very little sorption of atrazine and simazine to various chalks (Upper, Middle, Lower, Putty and Marl Band). Measured partition coefficients (K_d ml/g) range from 0.0308 to 0.205 for atrazine and 0.0287 to 0.358 for simazine. The lowest K_d 's have been measured for the 'white chalks' (Upper and Middle chalks) which form the bulk of the aquifer but also the most vulnerable. Slightly higher K_d 's have been measured for the Lower Chalk and Marl Band samples investigated.

Diffusion coefficients measured for atrazine and simazine within the Upper Chalk are in the order of 1×10^{-10} m²/sec, which are similar to a conservative tracer, bromide 2×10^{-10} m²/sec. Degradation of atrazine and simazine within the chalk is very slow as laboratory microcosms have revealed no degradation after a 100 day period. The half life of both compounds within the Chalk is expected to be at least 1000 days.

Modelling exercises have predicted that a thick (>10m) unsaturated zone can form an effective attenuation zone. These exercises have also shown that transport within fractures can be very rapid and if these become active within the unsaturated zone, during by-pass events, the attenuating capacity of the unsaturated zone is reduced thus allowing a more rapid infiltration into the aquifer. It is widely believed that by-pass mechanisms are responsible for the detections of both compounds within the aquifer. If this mechanism is responsible, then residues of both compounds are expected to drop below 0.1 µg/l quickly after the industrial ban on 31st August 1993, however, if matrix transport is responsible then residues will persist for some time.

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SUMMARY

The triazine herbicides, notably atrazine and simazine are the most commonly detected pesticide in ground waters from North America and Europe. Surveys by Anglian Water have revealed detections of atrazine in 28% and simazine in 9% of Chalk ground water samples (Croll, 1992). Understandably water companies are concerned with the detection rates for atrazine especially as its usage within UK agriculture is very low and the high cost of treatment facilities required to reduce concentrations to below the EC MAC. Typical concentrations found in public water supply boreholes are below $0.3\mu\text{g/l}$, with maximum concentrations just above $1\mu\text{g/l}$ (Croll, 1992).

This research project investigated why these two herbicides are so commonly found within the Chalk aquifer. The project used laboratory experiments to provide data on the sorption, degradation and diffusion of these chemicals. The results from these experiments will be related to field conditions during modelling exercises in order to evaluate the mobility and persistence within the aquifer.

The results obtained reveal very little sorption of atrazine and simazine to various chalks (Upper, Middle, Lower, Putty and Marl Band). Measured partition coefficients (K_d ml/g) range from 0.0308 to 0.205 for atrazine and 0.0287 to 0.358 for simazine. The lowest K_d 's have been measured for the 'white chalks' (Upper and Middle chalks) which form the bulk of the aquifer but also the most vulnerable. Slightly higher K_d 's have been measured for the Lower Chalk and Marl Band samples investigated. The rise in sorption is in response to the levels of organic carbon present within the samples ranging from 0.02% within the 'white chalks' up to 0.063% for the marl band sample.

Interestingly there has also been measurable sorption to mineral surfaces which has resulted in higher K_d 's than expected if partitioning to organic carbon only. Simazine shows this partitioning for the clay rich Lower and Putty Chalks and Marl Band samples, while atrazine only shows this for the Marl Band sample. Thus these samples will offer a greater attenuating capacity, but not great.

Using the measured K_d 's, matrix retardation factors calculated for the various chalks as expected are also low, again the lowest values obtained for the white chalks, while the highest being obtained for the Marl Band sample. The calculation of fracture retardation factors reveals that almost negligible retardation, due to sorption to fracture walls, will be expected.

Two transport mechanisms operate within the Chalk, these are matrix and fracture flow. Matrix flow is characteristically very slow and is the dominant transport mechanism within the unsaturated zone, while fracture flow is extremely rapid compared to matrix flow and is the dominant transport mechanism within the saturated zone. Occasionally fracture flow occurs within the unsaturated zone during periods of intense rainfall, or if a large volume of water from surface run off is collected into a concentrated entry point.

Apart from sorption, both diffusion and degradation will act to reduce any residues of atrazine and simazine present within the aquifer. As just mentioned sorption to fracture walls is insignificant, however, any residues present within the fracture will diffuse into the porous matrix. Diffusion coefficients have been measured for the Upper Chalk sample, ranging from $1.09 \times 10^{-10} \text{ m}^2/\text{sec}$ for simazine to $1.14 \times 10^{-10} \text{ m}^2/\text{sec}$ for atrazine. These values are in the same order of magnitude as a conservative tracer, Bromide ($2.29 \times 10^{-10} \text{ m}^2/\text{sec}$). These results indicate that the process of diffusion will be a rapid process for both atrazine and simazine. Further diffusion experiments are being performed with other chalks.

Degradation has been measured by the use of microcosm studies and have revealed no degradation over a 100 day period, which is consistent with other microcosm studies performed in North America and Denmark, on other aquifer materials. A trial microcosm set up last year has shown no degradation over a 360 day period. The only half life available for atrazine within aquifer materials is an estimated value of 1000 days (Perry, 1990), measured within a shallow contaminated aquifer in Nebraska, USA. The half lives of atrazine and simazine in Chalk are believed to be similar or possibly longer.

Using the experimentally measured sorption and diffusion coefficients some modelling exercises have been performed to assess the movement of the two herbicides within the chalk matrix and through fissures. These have shown that the short half lives commonly encountered in soils would result in negligible movement. Using the much higher half life reported by Perry (1990) resulted in greater distances of movement. These exercises did however, reveal that the unsaturated zone, in the absence of fracture flow, forms an effective attenuation zone with significant travel distances only being achieved at high input concentrations. However, the majority of large pumping stations are concentrated within valleys which are characterised by shallow water tables. Compounding this is that the major transport networks are concentrated within these same areas, so that the majority of applications will take place upon shallow unsaturated zones.

Modelling exercises conducted for fracture flow have revealed that at low flow velocities, long half lives are required to achieve any significant travel distances for both herbicides. However,

at higher flow rates greater travel distances (kilometres) are achieved even for rapid degradation rates. It is widely believed that the majority of water extracted from the aquifer originates from a few solution enlarged fissures which are characterised by very high flow velocities up to kilometres per day. At these velocities the effects of sorption, diffusion and degradation are insignificant, resulting in these fissures effectively forming pipes, allowing the rapid transport of atrazine and simazine through the aquifer.

These modelling exercises have also revealed that assuming a half life of 1000 days, it will take approximately eight years to attenuate residues of $1\mu\text{g/l}$ present within the chalk matrix to below $0.1\mu\text{g/l}$. For residues present within a fissure this will be more rapid due to the rapid transport and dilution that would be expected. Recent field evidence has shown that boreholes where regular detections above $0.1\mu\text{g/l}$ occur, have now fallen to below $0.1\mu\text{g/l}$, within one year of the non-agricultural usage ban enforced since 31st August, 1993 (Phil Aldous pers. comm. 1994). This would seem to indicate that the majority of atrazine and simazine was entering the aquifer through the fissure component and not the matrix.

In conclusion, this research has so far revealed that the chalk aquifer provides an ideal environment for the prolonged persistence of atrazine and simazine, namely little sorption or degradation. It seems likely that the reason why such low concentrations are detected is that very little of these two herbicides is entering the aquifer in the first place.

Key Words

Atrazine, simazine, Chalk aquifer, groundwater, adsorption, diffusion, degradation, half life, penetration depth, travel distance

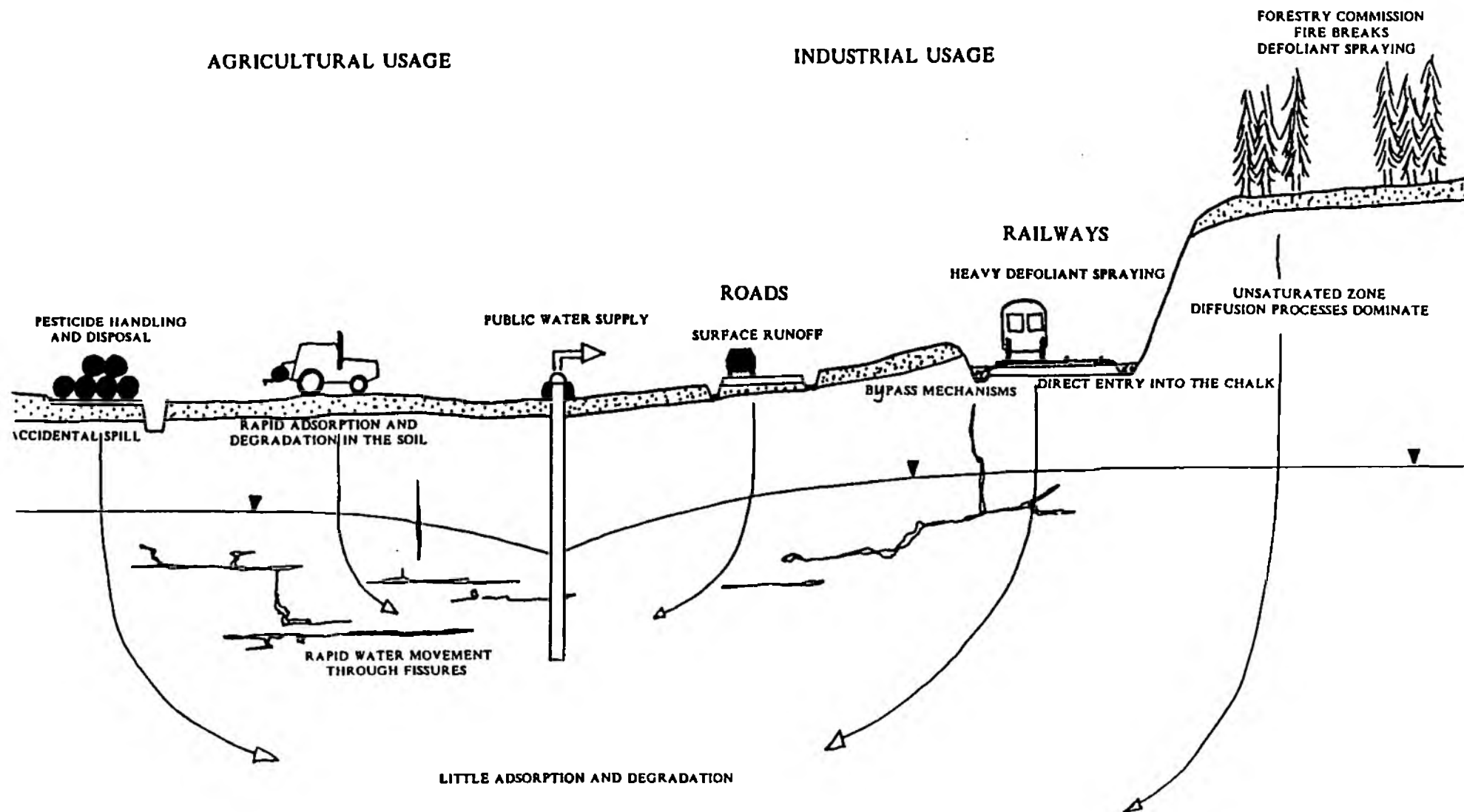
1 INTRODUCTION

The presence in drinking water of contaminants, both organic and inorganic, is undesirable on aesthetic, health and environmental grounds. The presence of pesticides, however, receives far greater media attention and public alarm than any other group of contaminants.

The triazine herbicides, notably atrazine and simazine, are the most commonly detected pesticides in ground waters from North America and Europe. The concentrations detected are very low, rarely exceeding $10\mu\text{g/l}$ in North America and $1\mu\text{g/l}$ in England and Wales. The EC drinking water Directive sets Maximum Admissible Concentrations (MAC's) of the $0.1\mu\text{g/l}$ for any pesticide and $0.5\mu\text{g/l}$ for total pesticides in water intended for human consumption (EC Directive No. 80/778/EEC).

Surveys by Anglian Water Services Ltd. have revealed detections of atrazine in 28% and simazine in 9% of sampled Chalk ground waters (Croll, 1992). The Chalk aquifer is the largest and most important aquifer in England, accounting for 15% of public water supplies in England and Wales. The majority of the aquifer is unconfined and covered by thin soils which support productive arable agriculture. The aquifer is dominantly composed of the Upper and Middle Chalks and to a lesser degree the Lower Chalk. The aquifer can be split into two physical units with respect to water movement, these being the unsaturated and saturated zones. Within these zones water moves in radically different ways; within the unsaturated zone water movement is dominantly by slow intergranular flow sometimes called 'piston displacement' and within the saturated zones rapid water movement can occur through the active fissure component. The unsaturated zone provides an important 'buffer' for the aquifer, however, the majority of abstraction wells are located in areas of shallow ground water and fissure flow is believed to occasionally occur within the unsaturated zone in response to intense periods of rainfall. These points are highlighted in figure 1.1, which provides a conceptual framework of the issues involved in the pollution of the chalk aquifer by atrazine and simazine.

The peculiar fact about the prevalent detections of atrazine and simazine is their minor use within UK agriculture. They are, though, some of the most heavily used herbicides for industrial purposes, especially transport. These activities, as well as populated areas, are concentrated within valleys. Valleys understandably have shallow ground water but they also possess some of the highest transmissivities found within the aquifer which are exploited by many abstraction wells. This combination of effects may explain the common detections of these two herbicides. In response to the concerns expressed by the water industry the UK government has banned the industrial use of atrazine since 31st August 1993.



Adapted from Foster *et al.* (1991)

Figure 1.1 Triazine usage and infiltration mechanisms within the Chalk aquifer

1.1 Objectives

The objective of this research is to investigate the behaviour of atrazine and simazine within the chalk aquifer, which has involved the following;

- (1) Laboratory experiments to measure the sorption, diffusion of both herbicides within various Chalks.
- (2) Modelling these results to see how these parameters effect the transport of atrazine and simazine within the matrix and fractures.
- (3) Interpretation of these results with data available in the literature in order to help predict the likely sources and future concentrations these two compounds within the chalk aquifer system.

Previous work on these herbicides has concentrated on behaviour within the soil environment and results from this work cannot explain the frequent occurrence of these herbicides within many aquifers from Europe and North America. No previous work has looked at the adsorption of atrazine and simazine to the chalk and only isolated work has been performed in the USA on other aquifer sediments.

1.2 Structure of report

Chapter two describes the experimental results obtained on the adsorption of atrazine and simazine to various chalks. These results have been used to calculate retardation factors. Chapter three describes the experimental results obtained on the diffusion of both compounds within Upper Chalk. These results have been used to calculate the diffusion coefficients expected within other chalks. Chapter four describes the experiment results obtained on the degradation of both compounds within the Upper Chalk and the data available on the degradation of atrazine and simazine within other aquifer sediments from North America and Europe.

Chapter five describes the modelling exercises that have been performed to assess the movement of both compounds within the chalk matrix and fractures. These results have then been used to assess the likely sources of the two compounds. Chapter six ties together the major issues concerning the contamination of the chalk aquifer by the triazine herbicides and discusses the importance of degradation on the residence of these two compounds within the aquifer.

2 SORPTION

2.1 Experimental technique

Chalk samples representing the various lithologies (Lower Chalk, Middle Chalk, Upper Chalk, Putty Chalk and Marl Band) were collected from north west Norfolk. The Marl Band, Lower, Middle, and Putty Chalk samples were collected from a worked chalk pit near Hillington (NGR TF.724249) and the Upper Chalk sample was collected from a worked pit near Hellhoughton (NGR TF.851273). These samples were kept in a dark cold room until being dried in an oven at 110°C for 3-4 days. After drying the samples were crushed using a fly press prior to milling into a flour using a Tema mill. The soil sample used in this study was collected by Dr Richard Andrews in 1989 from an agricultural field overlying the Middle Chalk, S.W. Norfolk (NGR not disclosed). This sample was stored in a dark cold room until oven dried by me. The resulting dry soil was then passed through a 2mm sieve and this fraction was used in subsequent batch experiments. The soil belonged to the Worlington/Methwold series of soils (Andrews, 1993), which are typically argillic brown sands and brown calcareous sands respectively (Soil Survey of England and Wales, 1984).

Batch experiments were performed using 25g of the powdered chalk samples or the sub 2mm fraction of the soil, with 25ml of spiked chalk ground water, which were agitated intermittently over a two day period. Controls containing only spiked ground water were performed for each concentration. All batch experiments were performed at room temperature (19-21°C). At the desired time the batches were centrifuged and the supernatant filtered before being passed through activated C18 solid phase cartridges. The C18 cartridges were activated using 5ml portions of methanol and acetone followed by 10ml of distilled water. After sample extraction the cartridges were then dried by passing air through them for 1 hour prior to elution using 5ml of acetone (removes atrazine only) followed by 5ml of dichloromethane (removes both atrazine and simazine). This sample was then blown to dryness under a stream of pure N₂ and then made up to the mark using acetone. Experimental samples were then analysed with calibration standards using propazine as an internal standard.

Analysis was performed on a Hewlett Packard HP 5890 gas chromatograph coupled to a HP 5970 mass spectrometer detector. the gas chromatograph (GC) was equipped with a fused silica capillary column, 25m, 0.2mm i.d. (HP1. 0.33µm film thickness), Hewlett Packard, USA. The GC column was coupled directly to the ion-trap manifold through the transfer line. The transfer line was maintained at 280°C. Helium was used as the carrier gas maintained at a head pressure of 15psi, resulting in a linear velocity through the column of 28 cm/s and a flow rate of 0.55ml/min. Splitless injections of 1µl were made using a HP 7693 auto liquid sample (ALS)

at an injection port temperature of 220°C. The oven temperature was maintained at for 1 minute and initially increased at 40°C/min to a temperature of 165°C, where a second ramp of 2°C/min continued to a maximum of 192°C. The septum purge vent was automatically opened after 75 seconds and the filament and multiplier were automatically turned on after 600 seconds (10 min). The ion trap detector was operated in selected ion monitoring mode with ion 200, 201 and 214 being atrazine's, simazine's and propazine's respective quantification ions.

2.2 Experimental results

Initial experiments were conducted to elucidate equilibrium times for interactions between atrazine and chalk. Sampling was conducted at 2, 5 and 10 days after mixing, with apparent equilibrium having been reached before two days. All except one experiment were performed at concentrations below 1000µg/L and the resulting isotherms were all linear over this concentration range. One experiment was performed with Putty Chalk to assess the sorption of atrazine at high concentrations up to 5000µg/l and this isotherm was also linear. Sorption isotherms for atrazine and simazine to various chinks and the agricultural soil are shown in Appendix 1. Experimentally derived partition coefficients are given in Table 2.1.

Table 2.1 Experimentally derived partition coefficients for atrazine and simazine with various chinks and a chalk soil

CHALK TYPE	f_{oc}	ATRAZINE			SIMAZINE			INSOLUBLE RESIDUE
		K_d	STD error	K_{oc}	K_d	STD error	K_{oc}	
Upper Chalk	0.000155	0.03077	±0.00305	199	0.028739	±0.00283	185	1.01%
Middle Chalk	0.000200	0.03584	±0.00432	179	0.037402	±0.00500	187	1.06%
Lower Chalk	0.000425	0.06917	±0.00812	163	0.100131	±0.00379	236	13.59%
Putty Chalk	0.000545	0.11396	±0.00294	209	0.285919	±0.01121	525	12.21%
Marl Band	0.000630	0.20513	±0.00663	326	0.358245	±0.00301	569	32.60%
Soil	0.006250	0.45088	±0.00685	72	0.390596	±0.00826	62	na

na = not directly applicable to soils as they are not a carbonate sediment. The measured clay(< 2µm) fraction for Worlington soils is 2% and for the Methwold soils is 7% (Soil Survey of England and Wales, 1984).

It can be clearly seen that all measured partition coefficients are small especially for the Upper and Middle Chinks. From these partition coefficients, K_{oc} values for the various chinks can be estimated using equation 2.1 (Karickhoff *et al.* 1979, and Schwarzenbach and Westall, 1981).

$$K_d = K_{oc} f_{oc} \quad (2.1)$$

where K_{oc} is the compound's partition coefficient to organic carbon and f_{oc} is the fractional organic carbon content. This relationship assumes that K_d is linearly proportional to f_{oc} and predicts the extent of partitioning when values of K_{oc} and f_{oc} are known.

Abundant information on the adsorption of atrazine and simazine to soils has been available in the literature for over 20 years. Mean K_{oc} values reported for atrazine in the literature range from 163 (Rao and Davidson, 1980) to 227 (Gerstl 1990). These mean values are based on literature surveys containing 56 soils and 217 values respectively. For simazine Rao and Davidson (1980) quote a mean K_{oc} of 138.4 from 147 soils and Gerstl (1990) quotes an average K_{oc} value of 104.7 from 240 values obtained from the literature.

The low sorption of atrazine to the various chalk samples used in this study are in keeping with the very limited number of published data available on other aquifer materials. These results with calculated K_{oc} values are shown in table 2.2.

Table 2.2 Published data on the sorption of atrazine to aquifer materials

Author	Aquifer / Sediment	K_d	f_{oc}	K_{oc}
Wehtje <i>et al.</i> (1983)	Ogallala Nebraska	0.40	-	-
		0.46	-	-
Nordmeyer <i>et al.</i> (1992)	Sand	0.2	0.0007	286
		0.1	0.0006	167
Agertved <i>et al.</i> (1992)	Borden/Ontario	0.04	0.0002	200

Also listed in Table 2.1 are some of the chemical properties that will effect the sorption of atrazine and simazine, namely organic carbon contents and the levels of clay minerals present (measured as insoluble residue, residues of quartz will also be present). The organic carbon contents were measured by Dr Brynn Jones at the University of Newcastle. Measured organic carbon contents and insoluble residues for the various chalks examined in this study, as expected, show that the lowest contents are present within the purer Upper and Middle Chalks. Much higher insoluble residues are present within the Lower and Putty chalks and markedly more residues are present within the marl band. Higher levels of organic carbon are also present within these samples.

A closer inspection of Table 2.1 reveals that calculated K_{oc} values for simazine increase in response to the levels of insoluble residues present within the Lower, Putty Chalks and Marl band sample. The only sediment for which atrazine shows this effect is the marl band. These samples are unusual when compared to the majority of chalks because of the high clay contents

present. If the partition model described by equation 2.1 was operating within all the chalks then constant, not rising K_{oc} values would be expected for atrazine and simazine.

2.3 Mineral phase sorption

It is proposed that mineral phase sorption is occurring to such a level that it has become measurable. The partition model described by equation 2.1 assumes sorption to organic carbon only. However, partitioning always occurs to both organic carbon and mineral fractions, with the organic carbon fraction dominating. In sediments containing very low levels of organic carbon the partitioning to mineral surfaces may become apparent. A conceptual framework can be used to differentiate between the mineral component and organic component of atrazine and simazine sorption to various chalks based on the following equation:

$$K_d = K_{oc} f_{oc} + K_m f_m \quad (2.2)$$

where K_m is the partition coefficient for the mineral fraction and f_m is the fractional mineral content of the sediment. K_{oc} and f_m are the same as before. K_m can be calculated if all the other parameters are known by rearranging equation 2.2 as follows

$$K_m = \frac{K_d - (K_{oc} f_{oc})}{f_m} \quad (2.3)$$

The various components required in equation 2.3 for the estimation of K_m can be estimated by assuming that sorption occurring in certain chalks is dominated by the organic carbon present. For atrazine it is assumed that all but the marl band sample exhibit this while for simazine only the Upper and Middle Chalks do. The mean K_{oc} values for these samples are then used as true K_{oc} . These mean K_{oc} values are 186.5 for atrazine and 186 for simazine. The distinction between the chalks which exhibit mineral phase sorption and the chalks can be clearly shown in figure 2.1 for atrazine and figure 2.2 for simazine. These figures are a plot of measured K_d with standard error against the organic carbon content of the chalks. Superimposed on this is a line representing the sorption expected solely to organic carbon. From equation 2.3, calculated K_m values for the various chalks which exhibit enhanced sorption coefficients are listed in table 2.3.

These measured K_m values are extremely small when compared to K_{oc} values and emphasise the low affinity of atrazine and simazine for mineral surfaces when compared to that for organic matter. The calculated K_m values for simazine show a wide variation with the highest value being associated with the Putty Chalk sample.

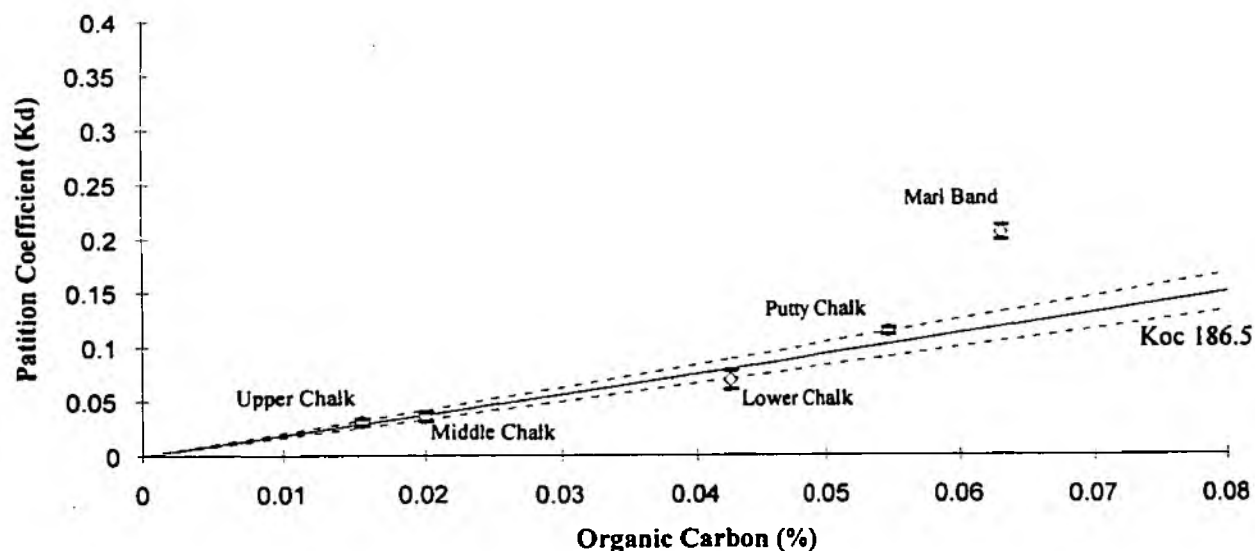


Figure 2.1 Comparison between experimentally derived partition coefficients for atrazine and that expected from partitioning to organic carbon only

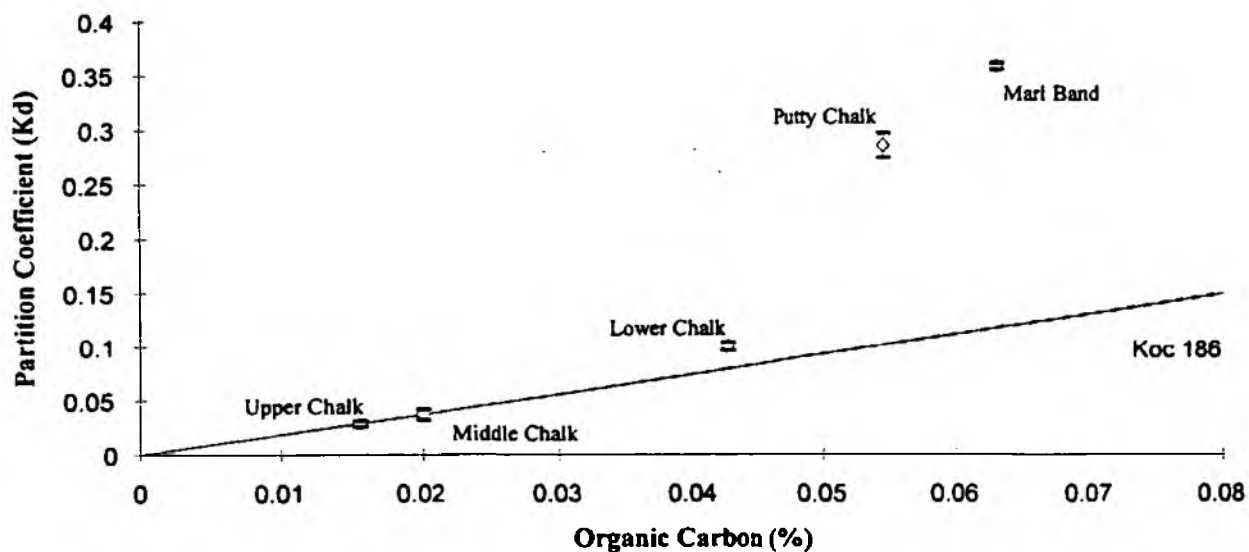


Figure 2.2 Comparison between experimentally derived partition coefficients for simazine and that expected from partitioning to organic carbon only

This variation in K_m values is probably due to the variable mineral compositions present within the insoluble residues from different chalks. If they had similar compositions then fairly constant K_m values would be expected.

Table 2.3 Calculated K_m (ml/g clay) values for the various chalks which exhibit sorption to mineral surfaces

CHALK	ATRAZINE	SIMAZINE
Lower Chalk	0	0.155
Putty Chalk	0	1.511
Marl Band	0.227	0.739

The present study has shown that mineral phase sorption can have a major effect on the sorption of these compounds in chalk sediments which contain high clay contents with low organic carbon contents. Table 2.4 shows this effect quite clearly for simazine, by using a mean K_{oc} value 186 obtained from the clay free Upper and Middle Chalks the estimated K_d 's for Putty Chalk and Marl Band are roughly three times less than actually measured K_d 's.

Table 2.4 Expected and measured sorption coefficients (ml/g chalk) for simazine to Putty Chalk and Marl Band

Chalk Type	Expected K_d	Measured K_d
Putty Chalk	0.10137	0.285919
Marl Band	0.11718	0.358245

Expected K_d = calculated K_d using equation 2.1 and a K_{oc} of 186.

Measured partition coefficients apply to both the matrix (saturated and unsaturated) and fracture walls.

2.4 Matrix retardation factors

Table 2.1 contains partition coefficients which indicate the degree of adsorption of the two herbicides to various chalks. Adsorption results in atrazine and simazine travelling at a slower rate than groundwater. The rate of their movement relative to groundwater can be determined by calculating retardation factors from the following equation.

$$R = 1 + \left(\frac{1-n}{n} \right) \rho_g K_d \quad (2.4a)$$

$$R = 1 + \frac{\rho_b}{n} K_d \quad (2.4b)$$

where, ρ_g is the grain density of pure calcite, ρ_b is the dry bulk density of the sediment and n the porosity.

Equation 2.4a is used when the bulk density of the sediment is unknown. The grain density of calcite is 2.715 g/cm^3 (Hancock, 1975). When the bulk density is known equation 2.4b is used. The soil has known dry bulk density of 1.2 g/cm^3 (Andrews, 1993). The porosities used for these calculations represent the measured value for the Upper chalk sample used and mean values for the Middle and lower Chalks presented by Price (1987). The porosities for the Putty chalk and Marl Band are not known nor are values available from the literature. It was decided to use the published Lower Chalk value as this deposit also has a high clay content. Table 2.5 shows the retardation factors that would be expected for the various chalks and the soil sample.

Table 2.5 Calculated Retardation Factors for atrazine and simazine within the various chalks

Herbicide	Upper Chalk $n = 0.38$	Middle Chalk $n = 0.33$	Lower Chalk $n = 0.25$	Putty Chalk $n = 0.25$	Marl Band $n = 0.25$	Soil $n = 0.40$
Atrazine	1.146	1.198	1.56	1.93	2.67	2.33
Simazine	1.137	1.206	1.82	3.33	3.92	2.17

It is interesting to note that the lowest retardation factors are expected within the Middle and Upper 'White' Chalks. These formations form the bulk of the chalk aquifer and any atrazine or simazine present within the matrix would be only slightly retarded with respect to water movement, moving at 83 - 88% of the groundwater velocity. As expected higher retardation factors are calculated for the more argillaceous chalks which are characterised by very low matrix flows and as a result they do not form important aquifer units. The marl band deposits transect the middle and upper chalks and will, therefore, offer sites for attenuation within these aquifer units as well as restricting flow across them.

The use of matrix retardation factors only describes the movement of a pollutant with respect to water flow within the matrix which is only of partial relevance with respect to water resources within the saturated zone as nearly all water moves through the dense fissure network present within the chalk. The calculated matrix retardation factors above are calculated for saturated conditions. However, the chalk matrix within the unsaturated zone approaches saturation (never less than 95%) even at very high pore water suctions, thus retardation factors calculated for the unsaturated zone will only be slightly greater than ones calculated for saturated conditions.

2.5 Fracture retardation factors

A solute present within a fracture will adsorb to the surface of the fracture wall. If the sorption to the fracture surface is considered to be linear it can be described by K_{fs} (the partition coefficient for the fracture surface), defined by Freeze and Cherry (1979) as the mass of solute adsorbed per unit area of surface (mg/m^2) divided by the concentration of a solute in solution ($\mu\text{g}/\text{l}$). the retardation factor for a fracture then becomes, (Freeze and Cherry, 1979)

$$R_f = 1 + \frac{K_{fs}}{\frac{1}{2}b} \quad (2.5)$$

where b is half the fracture aperture, and K_{fs} is the fracture surface partition coefficient.

The partition coefficients (K_d , mL/g) that I have obtained for the matrix can be converted to K_{fs} (m) if they are expressed as the mass sorbed per unit area of the disaggregated chalk used in the batch experiments. This approach must also be used if sorption to the fracture wall cannot be directly measured. Pacey (1983) reported a limited number of surface area measurements on samples from the Lincolnshire chalk with lowest surface areas being encountered within the Upper and Middle Chalks. The samples from the Lower Chalk had higher surface area values. Another aspect of the measurements taken from the Upper and Middle Chalks was an approximate increase in surface area of $0.1\text{m}^2/\text{g}$ per 5% rise in porosity. Using these surface areas my partition coefficients for each chalk type can be converted to K_{fs} which are shown in table 2.6. The Putty Chalk is excluded from these calculations as this deposit is rarely fissured.

Table 2.6 K_{fs} (m) calculated from measured K_d (mL/g) using the estimated surface areas for the various chalks

Chalk Type	Surface Area (m^2/g)	K_{fs} (m)	
		Atrazine	Simazine
Upper Chalk	1.8	1.71×10^{-8}	1.60×10^{-8}
Middle Chalk	1.4	2.56×10^{-8}	2.70×10^{-8}
Lower Chalk	2.1	3.30×10^{-8}	4.80×10^{-8}
Marl Band	12	1.71×10^{-8}	2.99×10^{-8}

The assumed surface area of the marl band is probably lower than would be expected for a clay rich deposit, but it is used in this situation to emphasise the effect that surface area has on retardation.

Calculated fracture retardation factors are extremely small and insignificant for both compounds. There is a slight increase in calculated retardation factors as the fracture aperture decreases, which would be expected given the nature of equation 2.5. However, values of R_f never exceeded 1.002, for the chinks considered, even marl bands. This is interesting as it is often thought that marl bands would offer important sites of attenuation by sorption, but is more likely that attenuation is achieved by such a deposit forming an aquitard to both water and any solutes present.

As well as sorption to fracture walls any solutes present within the fracture will diffuse into the highly porous chalk matrix.

3 DIFFUSION

As mentioned in the previous chapter a solute present within fractures will diffuse under a concentration gradient into the porous matrix. This will act to reduce concentrations within a fracture, in effect slowing the movement of the solute within the fracture. However, once concentrations within the fracture have fallen then diffusion from the matrix back to the fracture will occur, in so doing prolonging the persistence of the pollutant. Thus the process of diffusion is extremely important within the Chalk and the use of diffusion coefficients allows the quantification of the fracture-matrix transfers.

Using the method performed by Hill (1989), diffusion cell experiments performed with disks cut out of blocks of the Upper chalk sample used for the batch experiments. Measured effective diffusion coefficients (D^*) for atrazine, simazine and bromide are given in the following table.

Table 3.1 Measured effective diffusion coefficients for the Upper Chalk

Chemical Species	Effective Diffusion Coefficient
Atrazine	$1.137 \times 10^{-10} \text{ m}^2/\text{sec}$
Simazine	$1.086 \times 10^{-10} \text{ m}^2/\text{sec}$
Bromide	$2.288 \times 10^{-10} \text{ m}^2/\text{sec}$

Porosity = 38%

Temp = 19.6°C

The effective diffusion coefficient can be calculated for the remaining chalks by using the following equation,

$$D^* = \left(D_o \frac{n}{\tau} \right) / R \quad (3.1)$$

where; D_o is the free diffusion coefficient (diffusion coefficient in pure water), n is the matrix porosity, τ is tortuosity and R is the retardation factor for the matrix. Tortuosity is measure of the effect of the shape of the flowpath followed by molecules in a porous media. If L is the straight-line distance between ends of a tortuous flowpath of length L_e , the tortuosity can be defined as $\tau = L_e/L$. Tortuosity in a porous media is always greater than 1, because the flowpaths that molecules take must diverge around solid particles.

Scott and Philips (1973) measured free diffusion coefficients of $6.6 \times 10^{-10} \text{ m}^2/\text{sec}$ for atrazine and $5.8 \times 10^{-10} \text{ m}^2/\text{sec}$ for simazine at 23°C. The free diffusion coefficient for bromide is $17.6 \times 10^{-10} \text{ m}^2/\text{sec}$ at 25°C (Lloyd and Heathcote, 1985). Retardation factors and porosities for the

matrix are given in table 2.5. Tortuosity at various porosities has been estimated by analysing the data from Hill (1984) and reveal values of τ ranging from 2 at porosities of 0.4, rising up to values of 9 as porosities drop to below 0.2. After correcting the free diffusion coefficients to a temperature of 19.6°C, effective diffusion coefficients have been calculated using equation 3.1 for the types of chalks not measured and are shown in Table 3.2.

Table 3.2 Calculated effective diffusion coefficients D^* ($\times 10^{-10} \text{m}^2/\text{sec}$) for atrazine, simazine and bromide for various chalks at 19.6°C

Chemical	Middle Chalk $n = 0.33$	Lower Chalk $n = 0.25$	Putty Chalk $n = 0.25$	Marl Band $n = 0.25$
Atrazine	0.451	0.136	0.111	0.0790
Simazine	0.393	0.103	0.056	0.0048
Bromide	1.741	0.688	0.688	0.688

These calculated effective diffusion coefficients are similar to the values measured by Hill (1984) for tritium, nitrate and chloride in uncracked chalk.

4 DEGRADATION OF ATRAZINE AND SIMAZINE WITHIN AQUIFER SEDIMENTS

4.1 Previous work on soils and non-Chalk aquifer materials

Much research has been performed on the degradation of atrazine and simazine within soils. Rao and Davidson (1980) from an extensive literature survey quoted mean half lives of atrazine and simazine in soils of 48 and 70 days respectively. The degradation of atrazine within aquifer sediments has recently been investigated by several workers (Agertved *et al.*, 1992; Klint *et al.*, 1993; McMahon *et al.*, 1992; Perry, 1990; Wehtje *et al.*, 1983; and Wood *et al.*, 1991). No such studies have been performed for simazine within such sediments. The majority of these studies have used laboratory microcosms to measure the rate of degradation.

Wehtje *et al.* 1983 and Agertved *et al.* (1992) failed to measure any degradation of atrazine over a 70 day period in laboratory microcosms containing aquifer sediments. An intensive laboratory microcosm study was performed by Klint *et al.* (1993) using ground water only and aquifer/groundwater mix. These experiments showed no degradation of atrazine over a 539 day period within the ground water only experiments and a 174 day period within the aquifer material/ground water mix. Incubation at either 21°C or 10°C, or the addition of nutrients had no effect on the lack of degradation. However, partial removal of atrazine was observed after the addition of 3g of fresh topsoil to one of the microcosms. In this microcosm the concentration of atrazine was reduced from 100µg/l to about 50µg/l in 30 days whereafter no further degradation was observed. Agertved *et al.* (1993) also found no degradation of atrazine during a 160 day field natural gradient test, nor during a 47 day field in situ experiment.

Perry (1990) reported field investigations of a shallow sand aquifer in Kansas polluted with the herbicides atrazine, alachlor, cyanazine, metolachlor and metribuzin. A three year investigation of this site revealed the slow decline in the concentration of atrazine, when extrapolated resulted in an estimated half life of 1000 days. Early sampling of this site revealed roughly equal concentrations of atrazine and metolachlor (>30µg/l), however, the concentrations of metolachlor declined much more rapidly than those of atrazine. The half life of metolachlor was estimated to be 350 days. A laboratory study performed by McMahon *et al.* (1992) reported mineralisation rates of <0.1-1.5% of added [*ethyl*-2-¹⁴C]atrazine in 23 days. When these mineralisation rates are extrapolated they result in calculated half lives of between 11,500 to 767 days which are in the same time scale as those reported by Perry (1990) and seem to support the recalcitrant nature of atrazine within aquifer sediments.

4.2 Previous work on Chalk

Contrasting this picture are the results obtained by Wood *et al.* (1991). These workers investigated the degradation of atrazine within groundwater and sediments collected from the London Basin. They observed half lives for atrazine in chalk groundwater ranging from 114 to 123 days. Also microcosms were performed containing sediments from two U100 cores sunk by the BGS. These experiments were performed using 5g of sediment (Woolwich and Reading Beds, Thanet Beds and Putty Chalk) and 10ml of the chalk groundwater. These samples were analysed after 24 weeks and revealed almost complete removal of atrazine (94.6->99.7%) from the Woolwich and Reading Beds and Thanet Beds. Samples containing Putty Chalk only showed partial removal (40-54.3%) of atrazine.

These results are in stark contrast to the results obtained by the other studies discussed above. Either the microbial population present within the sediments of the London Basin are especially adapted to degrading atrazine or the experimental technique used encourages enhanced microbial activity. A clue could be the high concentrations used during these experiments. The groundwater experiment used atrazine at a concentration of above 5mg/l, while the sediment/groundwater experiments used saturated (~30mg/l) concentrations of atrazine. Typical concentrations of naturally occurring dissolved organic carbon (DOC) present within chalk groundwaters rarely exceed 0.55mg/l (Kenrick *et al.* 1985) which is significantly lower than the concentrations used by Wood *et al.* (1991). At these high concentrations atrazine could provide the primary source of organic carbon to metabolising bacteria. Boething and Alexander (1979) and Rubin *et al.* (1982) noted that the results from degradation studies in soil with high concentrations of pesticide cannot always be extrapolated to oligotrophic aquifer environments where the pesticide concentrations may be too low for biodegradation to be initiated. The use of such high concentrations by Wood *et al.* (1991) is probably initiating microbial metabolism of atrazine and is also not representative of concentrations found within the chalk aquifer.

4.3 Project experiments and results

Eleven laboratory microcosms have been constructed, six containing 2kg of wet chalk (~1.5kg dry) and 3L of Chalk groundwater and five microcosms containing 3L of groundwater only. One microcosm from each set has been sterilised by autoclaving and will act as controls. All microcosms were constructed under aseptic conditions within 5 days of fresh chalk and groundwater collection and are stored in dark basement at temperatures below 16°C. The whole experiment was constructed on the 31st April 1994 and will run until the end of the year,

during which several bottles will be amended with nutrients if no degradation is taking place. Preliminary results show no degradation of atrazine and simazine over a 103 day period.

A trial microcosm was earlier constructed in April 1993. This consisted of 1.5kg of wet chalk and 2L of groundwater contained within an old amber solvent bottle. The chalk and groundwater were both old, with the chalk having remained in my office open to the atmosphere and allowed to dry. The chalk groundwater was collected on 24/3/92 and has remained in store within a fridge at 5°C. This microcosm has been used to assess the possibility of microbial contamination from the techniques used to construct the microcosm and contamination during the running of the experiment. This experiment failed to detect any degradation over a 380 day period.

4.4 Conclusions

These laboratory and field experiments have revealed that there is little potential for the rapid degradation of atrazine within aquifer sediments including the Chalk. Half lives for atrazine and simazine within the Chalk aquifer are expected to be in the order of thousands of days at realistic concentrations.

5 MODELLING

Using the experimental results obtained, various analytical solutions have been performed to assess the movement of atrazine and simazine within the Upper Chalk. The two transport mechanisms which operate within the Chalk are matrix and fracture flow. Matrix flow is characteristically very slow and is the dominant transport mechanism within the unsaturated zone, while fracture flow is extremely rapid compared to matrix flow and is the dominant transport mechanism within the saturated zone. Occasionally fracture flow occurs within the unsaturated zone during periods of intense rainfall, or if a large volume of water from surface run off is collected into a concentrated entry point.

Separate analytical solutions will be used to describe each of these transport mechanisms. For matrix flow, penetration depths will be calculated. This is the depth below the input horizon at which the concentration of atrazine and simazine has fallen below 0.1µg/l from various input concentrations. These penetration depths provide information on the effectiveness of the unsaturated zone (in the absence of fracture flow) to attenuate both compounds but will also provide clues to the likely degradation rates to be found. This is because the slow movement of water will allow ample time for degradation to occur.

For fracture flow, travel distances are calculated. These are the distances along a fracture by which the concentration of atrazine and simazine have fallen below 0.1µg/l from various input concentrations. These travel distances are calculated for a set of fractures with a defined aperture and spacing, with diffusive losses into the porous matrix. The travel distances for this system are influenced by the half lives of the compounds and most importantly the velocity of the water within the fracture.

5.1 Matrix transport

A simple steady state analytical solution can be used to look at the effect of sorption and various half lives on the penetration depth of atrazine and simazine within the unsaturated zone of the Upper and Middle Chalks. This steady state solution is (Domenico and Schwartz, 1990)

$$C = C_0 \exp \left\{ \left(\frac{x}{2a_x} \right) \left[1 - \left(\frac{1 - 4\lambda a_x}{v/R} \right)^{1/2} \right] \right\} \quad 5.1$$

Where, x is depth, a_x is dispersion coefficient, λ is the decay constant ($\lambda = \ln 2/\text{half life}$), v is ground water velocity and R is the matrix retardation factor.

Equation 5.1 describes one dimensional advective, dispersive transport with reaction (sorption and decay). The penetration depth of atrazine and simazine can be calculated using the matrix retardation factor of 1.15 for the Upper Chalk, various half lives reported for the soil (48 days) and aquifer sediments (1000 + days) and an advective velocity of 0.7m/pa, which is high for East Anglia. Depending upon the amount of effective rainfall, advective velocities within the unsaturated zone vary from <30cm/a during the 1989-1992 drought (Andrews, 1993) up to 1m/a (Smith *et al.* 1970). The effective rainfall for East Anglia is on average less than 180mm/a, so infiltration rates will rarely exceed 0.7m/a within the region.

Table 5.1 shows the penetration depth at which various constant input concentrations of atrazine and simazine would be attenuated to below 0.1µg/l, using the values described above. The input concentration of 33,000µg/l represents the solubility of atrazine. The values in table 5.1 also apply to simazine up to its solubility of 5000µg/l.

Table 5.1 The effect of half life on the penetration depths of atrazine for various input concentrations

Input Concentrations (µg/l)	Half Life	
	48 days	1000 days
1	0.28	5.6
10	0.55	11.2
100	0.82	16.7
1,000	1.08	22.5
33,000	1.49	30.8

Using the average soil half life for atrazine reported by (Rao and Davidson, 1980), it can be clearly seen that there is a negligible depth of penetration even at concentrations approaching the solubility of atrazine and simazine. For matrix flow to achieve the concentrations reported within the aquifer a much longer half life is required. Using the 1000 day half life a more realistic picture appears with penetration depths exceeding 20m when input concentrations of 1000µg/l are used. Recently published data (Croll 1992) reveal an association between boreholes in which regular detections of atrazine above 0.1µg/l occur and high levels of nitrate (>50mg/l). The high levels of nitrate are indicative of shallow young groundwaters and tie in with the penetration depths achieved when using long half lives.

This analytical solution not only gives a measure on the effectiveness of the unsaturated zone but also an indication of the slow or negligible rates of degradation present within the aquifer. The slow rate of water movement allows ample time for degradation to occur. If a long half

life of 1000 days is correct, then high input concentrations are required to achieve significant penetration depths through the unsaturated zone, and a thick unsaturated zone would provide an effective attenuation zone. However, alternative mechanisms could explain the observed concentrations; (a) even slower rates of degradation, (b) the major abstraction wells are concentrated within valleys where shallow water tables are present or (c) concentrated inflows by-passing the matrix. These are discussed again in chapter 6.

5.2 Fracture transport

As mentioned above fracture flow is the dominant transport mechanism below the water table, however it occasionally occurs within the unsaturated zone during periods of intense rainfall. This fracture flow allows water and solutes to by-pass the matrix and rapidly enter the saturated zone, in so doing diminishing the attenuating capacity of the unsaturated matrix.

A steady state analytical solution is available to calculate the travel distance of atrazine and simazine along a fracture within a porous matrix. This analytical solution takes into account diffusion into the matrix. The ultimate travel distance of a contaminant at a concentration $c/c_0 = \delta$ along a fracture is (Sudicky and Frind, 1982)

$$d_\delta = \frac{\ln \delta}{(R_f \lambda / v) (1 + \beta)} \quad 5.2$$

where R_f is the fracture wall retardation factor, λ is the decay constant, v is the fissure water velocity, d_δ ultimate travel distance and β is the matrix sink term, given by;

$$\beta = \frac{\theta (D^*)^{1/2}}{\lambda^{1/2} b R_f} \tanh (\sigma \lambda^{1/2}) \quad 5.3$$

where, θ is matrix porosity, D^* effective diffusion coefficient, R is matrix retardation factor, b is half the fracture aperture and σ is the matrix block to fracture spacing relationship, given by;

$$\sigma = G (B - b) \quad 5.4$$

where B is half the matrix block size and G is given by;

$$G = (R/D^*)^{1/2} \quad 5.5$$

The fracture network of the chalk can be split into two distinct hydraulic groups, known as the 'primary fissure component' and the 'secondary fissure component'. The primary fissure component comprises of a wide range of fissure sizes up to the millimetre scale and form a dense orthogonal network within the chalk matrix. Superimposed on this network is the secondary fissure component, which comprises solution enlarged fissures up to the centimetre scale, with wide spacing and concentrated within the zone of water table fluctuation. These fissures have the capacity to transmit large volumes of water extremely rapidly through the aquifer. Patsoules and Cripps (1990) surveyed the primary fissure component of the Yorkshire chalk and reported fracture apertures ranging from 100 to 600 μm , with median values around 300 μm . Typical spacing for these fissures is approximately 14cm.

The use of the primary fracture component allows us to estimate the effect of movement within fractures. This component is expected to be responsible for fracture flow that occasionally occurs within the unsaturated zone, as these are the first fissures to saturate. The results obtained from this analysis will allow comparisons with the distances achieved for matrix flow.

Using equation 5.2 the effect of sorption, diffusion, degradation and fissure water velocity on the travel distance achieved for atrazine and simazine within the primary fissure component were calculated. These travel distances were calculated for a constant input concentration of 10 $\mu\text{g/l}$ to be attenuated to below 0.1 $\mu\text{g/l}$ within fractures with apertures of 300 μm and spacing of 0.14m contained within the Upper Chalk. Calculated travel distances for the primary fissure component at various half lives are shown in figure 5.1. Figure 5.1 shows that at very low fracture water velocities very long half lives are required for any significant travel distance to be achieved. At very low velocities the travel distance are comparable to the depths achieved by matrix flow only. However, as the fissure water velocity rises the travel distance is significantly greater. At velocities of 100m/d the use of very short half lives still results in great travel distances achieved.

If one assumes that typical travel distances to boreholes are of the order of 1km, then at a half life of 1000 days a fissure water velocity of 30m/d is required for a 10 $\mu\text{g/l}$ source concentration to contaminate this borehole. This critical fissure water velocity will decrease if longer half lives are present within the aquifer and vice versa.

The use of water velocities in the order of 100m/d are unrealistic for the primary fissure component, but are used to emphasise the importance of velocity on the travel distances achieved by atrazine and simazine. Velocities of this order and greater are found within the secondary fissure component with their associated larger apertures.

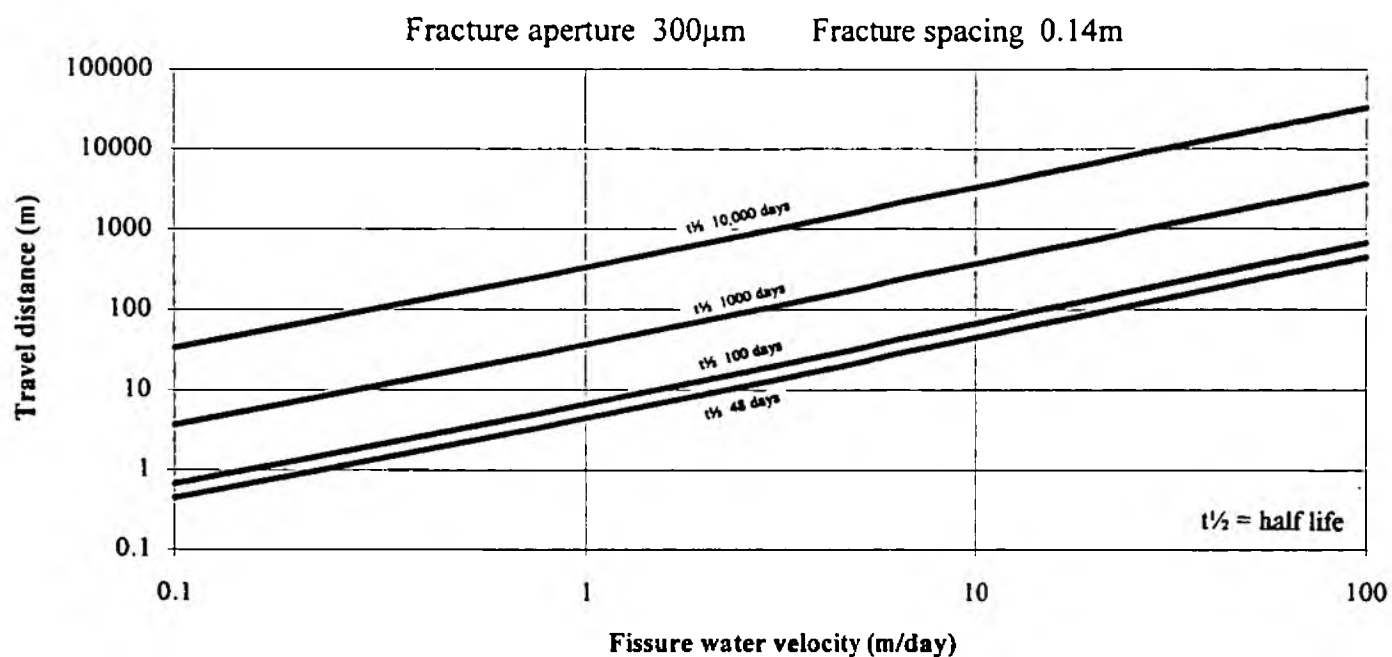


Figure 5.1 The travel distance of constant input concentration of 10 μ g/l of atrazine or simazine to be degraded to below 0.1 μ g/l within primary fractures at various fissure water velocities

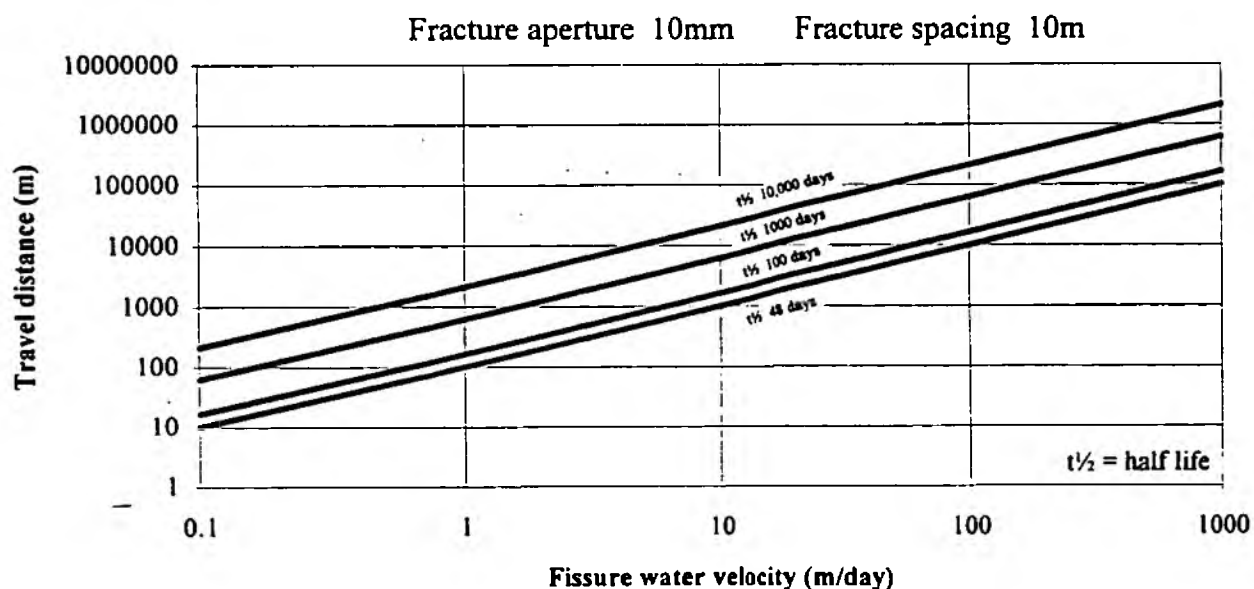


Figure 5.2 The travel distance of constant input concentration of 10 μ g/l of atrazine or simazine to be degraded to below 0.1 μ g/l within the secondary fissure component at various fissure water velocities

The majority of these fissures are present within the zone of water table fluctuation, which is a narrow zone within the aquifer where the water table rises and falls in response to seasonal variations in recharge. This zone is specifically exploited by water supply boreholes, which under the influence of pumping draw in water present within the fissures at high velocities in the vicinity of the borehole. This velocity is related to the pumping rate and declines away from the borehole. For example the M1/M25 interchange study reported a straight line groundwater velocity of 600m/d in one of their tracer test (Price *et al.* 1989) and velocities as high as 2.2 km/d have been reported (Atkinson and Smith, 1974). Effectively these large fissures form pipes allowing almost limitless movement of both compounds within the aquifer. This is shown in figure 5.2, where the high fissure water velocities effectively render the attenuating effects of diffusion into the matrix and decay insignificant. This system uses a fracture aperture of 10mm as reported by Ward *et al.* (1968) and a fracture spacing of 10m.

If fracture flow does occur within the unsaturated zone it will be confined to the small aperture fractures of the primary fissure component. A fracture of aperture 300 μ m could naturally conduct water at 1m/d through the vertically unsaturated zone. If atrazine or simazine were present at a concentration of 10 μ g/l then at this velocity the travel distance would be 37m, which is much greater than the penetration depth of 11.2m achieved through the matrix alone. The secondary fissure component will rarely become active within the unsaturated zone.

6 DISCUSSION

This chapter discusses the experimental and modelling results in the context of the usage of atrazine and simazine and their possible behaviour within the aquifer. Both atrazine and simazine are only occasionally used within agriculture, but were extensively used within industry prior to their ban on 31st August 1993. The agricultural applications will be to the soil, while many industrial applications will take place to impervious surfaces and directly to the chalk present within cuttings.

6.1 Entry mechanisms and behaviour within the chalk aquifer

The soil horizon provides an effective attenuation zone with atrazine and simazine readily adsorbing to organic matter, resulting in mean soil K_d 's of 3.2 ($n=56$) and 2.3 ($n=147$) respectively (Rao and Davidson, 1980). Once within the soil they rapidly degraded by soil micro-organisms resulting in short half lives, mean values ranging from 33 to 47 days for atrazine and 71 to 95 days for simazine (Rao and Davidson, 1980). These statements are generalisations as the soil investigated during this research had a K_d of only 0.45 which is much lower than an average soil. This sample was very sandy and probably represents a worst case soil. This is exacerbated by the fact that the calcareous soils which cover the chalk aquifer are also thin. The soil used in this study was taken from a site where weathered chalk was reached at about 0.7m.

Typical agricultural applications are applied at rates of between 1.5 kg/ha to 4 kg/ha, which equates to between 150mg/m² to 400mg/m². Assuming that these concentrations are evenly incorporated into the top 15cm of a metre square area of the soil then the concentrations will range from 0.83mg/kg up to 2.22mg/kg. This is calculated using a soil density of 1.2g/cm³. These concentrations are then available to undergo sorption processes with the soil, absorption by plants and degradation, both microbial and chemical.

Wehtje *et al.* (1983) conducted field lysimeter experiments on a plot of sandy soil which received an application of atrazine at a rate of 1.6 kg/ha. These lysimeters were also under centre pivot irrigation so high infiltration rates would be expected through the soil to the underlying aquifer. Under these conditions only 5.5g/ha of atrazine was measured entering the aquifer. This equates to only 1.98µg/l atrazine leaving the soil horizon and represents a 290 fold decrease in concentration. This situation is not very realistic as the soils present on the outcrop will be unsaturated for most of the year. It is used as an upper limit to infiltrating concentrations in the calculations below. Within an unsaturated soil the majority of the pore spaces will be occupied with air so greatly reducing the hydraulic conductivity. This low water

content will also concentrate the amount of atrazine or simazine present within it and in so doing more of the herbicides will be sorbed to the soil. The residence time within the soil will allow opportunity for microbial degradation to significantly reduce the concentrations present.

An inspection of table 5.1 reveals that an input concentration of $1.9\mu\text{g/l}$ will not penetrate a significant depth ($>5\text{m}$) in the presence of even a slow rate of degradation. This indicates that leaching of agricultural applications of atrazine and simazine under natural infiltration is expected to be minimal.

Problems do arise, however, where fracture flow occurs within the unsaturated zone as a result of intense rainfall or surface run off. As mentioned within chapter 5 the penetration depth of $10\mu\text{g/l}$ of atrazine or simazine will only travel 11.2m via matrix flow only and a slow rate of degradation. However, if the primary fissure component becomes active within this zone the same concentration can travel a distance of 37m , in effect offering a bypass of the attenuating capacity of the matrix. This unsaturated zone fracture flow allows a rapid transport mechanism to the saturated zone and is believed to be responsible for the detections of both herbicides within the aquifer.

Surface run off from a large area is often concentrated into a small area such as a drain, which then takes the water away to a river or into the ground. Surface runoff, even from low intensity rainfall, will increase the likelihood of induced fissure flow within the unsaturated zone. Industrial applications of atrazine and simazine are usually done at high dosages (up 20 kg/ha). Many of these applications take place on areas where runoff concentrates and by-pass mechanisms operate, as in road side ditches where cracks and macropores can occur as a result of soil shrinkage. Most importantly of all many such applications take place in cuttings, where the soil has been removed, so allowing direct entry into the chalk. The importance of runoff drainage from large surface areas cannot be underestimated as the chalk outcrop supports a large number of NATO airbases in East Anglia.

Once atrazine has been able to pass through or by-pass the soil horizon it will enter an environment vastly different to that of the soil. The environment of the chalk aquifer has a pH range 7-8, very low levels of organic matter and variable amounts of clay. There will also be a low microbial population density which is adapted to oligotrophic conditions. These conditions represent an environment which is not conducive to rapid degradation and where the chloro-triazines are at their most stable.

The lowest partition coefficients of atrazine and simazine were measured for the Upper and Middle Chalk, which form the vast majority of the aquifer due to their areal extent. However,

the heterogeneity of the chalk aquifer must be taken into account as there are many marl bands present which have much higher clay and organic contents. Areas of the chalk also contain periglacially reworked chalk called "putty chalk" which has a putty like texture, low hydraulic conductivities and variable clay contents. The lower chalk has higher clay contents and organic matter contents than the middle and upper chalks. These will represent potential areas of increased sorption and reduced movement.

Matrix flow within the interfluvial areas will result in minimal pollution potential by atrazine and simazine. However, these areas do not form important aquifers due to the low transmissivities often found in these areas and the above theory relies on matrix flow alone. During short periods of intense rainfall and surface runoff events from an airfield, the fissure component within the unsaturated zone may become active so facilitating a more rapid infiltration mechanism. Notwithstanding these mechanisms the depth of the unsaturated zone is very important in determining the susceptibility of the aquifer to pollution. The highest published concentration of atrazine and simazine in a public supply well is 1.3 and 1.2 µg/l respectively (Croll, 1992). An inspection of table 5.1 reveals that these concentrations are most likely to occur in areas of shallow ground water and that a water table below an unsaturated zone depth of 10m or more will be unlikely to become contaminated. This does though assume, as before, matrix flow only and a slow degradation rate.

The major abstraction points are associated with areas of high transmissivities which are concentrated within valleys. Obviously, these areas possess shallow unsaturated zones so only limited attenuation is available. To compound this most of the major transportation networks as they cross the outcrop are situated in valleys along with populated areas. This situation will provide a worst case scenario.

On quickly reaching the saturated zone any residues will enter the active fissure water, where ground water velocities are much higher than within the matrix, especially within the solution enlarged fissures present within the zone of water table fluctuation. Diffusion is a very important process within the chalk and any solutes present within the active fissure water will readily diffuse into the surrounding matrix. For a given fissure water velocity the penetration depths for atrazine and simazine, calculated using equation 5.2, revealed that without the process of diffusion, penetration depths were two and a half orders of magnitude greater than with diffusion occurring. However the retardation of atrazine and simazine by diffusion into the matrix and degradation is insignificant when high fissure water velocities are present. This is exactly the situation present within the solution enlarged fissures, which are believed to contribute the majority of water extracted by boreholes.

This points to one question, why isn't more atrazine or simazine found within the aquifer? The answer may be the low usage of these two compounds within England and Wales. Very little atrazine or simazine is used within agriculture, however, the industrial usage was much greater with 138 tonnes of atrazine and 76 tonnes of simazine applied annually (DoE report, 1991). These applications are for the country as a whole so only a small proportion will be applied directly to the chalk outcrop area. Since the ban on the industrial usage of atrazine came into force on the 31st August 1993, the use of this herbicide is now practically minimal. This leaves the question of how long the residues of atrazine present within the aquifer will remain.

6.2 Future concentrations within the aquifer

The assumed half life of >1000 days would seem to indicate a possible problem in the removal of any residues. However, observed concentrations of atrazine currently present within the aquifer are very low, so removing this as a possible problem. A hypothetical spillage or leakage of a storage tank or disposal site will offer a much greater problem. As sorption is only a minor attenuating mechanism any high concentration residues will require a long time to be degraded naturally. Such a polluted site would require restoration most probably by pump and treat. As sorption is minimal the majority of atrazine or simazine will be present within the aqueous phase so allowing easy withdrawal from the aquifer. A problem may occur with the residues which have diffused into the matrix. These will require longer periods of time to diffuse back out of the matrix and into the fissure water which can easily be removed.

The mode of entry into the aquifer may hold the key to predicting future detection rates of atrazine and simazine within water supply boreholes. If atrazine and simazine were entering the aquifer via by-pass movement through the fissure component then a rapid fall off in concentrations would result. This is because there is little storage of residues present within the chalk matrix and the repeated application of atrazine and simazine to the surface keeps concentrations up within infiltrating water. However, if matrix transport was responsible for the infiltration of both compounds, then a different pattern will result. The slow movement of water within the matrix also only allows the slow release of chemicals to the fissure component within the saturated zone. So a sudden stop to the application of atrazine and simazine at the surface will not result in a sudden drop off in concentrations encountered within the aquifer.

Recent field evidence has shown that boreholes where regular detections above 0.1 µg/l occur, have now fallen to below 0.1 µg/l, within one year of the non-agricultural usage ban enforced since 31st August, 1993 (Phil Aldous pers. comm. 1994). This would seem to indicate that the majority of atrazine and simazine was entering the aquifer through the fissure component and

not the matrix, thus supporting the by-pass hypothesis. However, there is as yet not enough field data to available to fully support this argument.

If such field evidence becomes available it could help in determining which entry mechanism was operating at a particular site. Obviously boreholes where residues of atrazine and simazine have fallen to below $0.1\mu\text{g/l}$ since the ban were contaminated by rapid by-pass mechanisms. Sites where residues are still present at above $0.1\mu\text{g/l}$, since the ban, would indicate either residues present within the unsaturated zone, left as a legacy to industrial applications or may still be receiving fresh inputs from agricultural activities.

7 CONCLUSIONS

- (1) Experimentally measured partition coefficients for both atrazine and simazine are small for all the chalks investigated, with the lowest measured on the Upper and Middle Chalk samples which form the major aquifer units. Mean K_{oc} values for atrazine and simazine to the chalks in which sorption is dominantly to organic carbon are 186.5 and 186 respectively.
- (2) The sorption to mineral surfaces was found to account for the inflated sorption of atrazine to the Marl band deposit and the sorption of simazine to the Lower chalk, Putty chalk and Marl band also. This scale of this mineral phase sorption was larger than expected and will offer greater attenuation. Calculated K_m values for simazine to the chalks which exhibit measurable sorption to mineral surfaces reveal a great variation between lithologies. This is expected to be the result of differing clay mineral compositions present within the insoluble residues.
- (3) Calculated retardation coefficients for matrix flow are small, even for the more argillaceous deposits. Calculated retardation factors for fracture flow are insignificant in the absence of diffusion.
- (4) The process of adsorption is not a very important attenuating mechanism for atrazine and simazine within the chalk aquifer.
- (5) The few published data and my experiments on the degradation of atrazine within aquifer sediments suggest that degradation is not a rapid process. The same is expected for simazine.
- (6) The diffusion of atrazine and simazine is calculated to be close to those of nitrate and chloride measured by Hill (1984). The rate of diffusion is controlled by the porosity of the media and the degree of retardation, so highest diffusion coefficients are expected within the Upper and Middle Chalks, whilst the lowest are expected within Marl Bands and Putty Chalk.
- (7) Modelling exercises have shown that matrix flow within the unsaturated zone can form an effective attenuation zone to diffuse inputs. Modelling has also shown that fissure flow will provide a rapid and unhindered transport mechanism within the Chalk aquifer, even with the effects of diffusion and degradation.

- (8) The experimental and modelling results justify the banning of atrazine and simazine from industrial usage.
- (9) Concentrations of atrazine and simazine are expected to drop fairly quickly after the industrial usage ban, due to the flushing of fissures even if the rate of degradation is slow and slow back diffusion into the fissures of residues within the matrix.

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APPENDIX

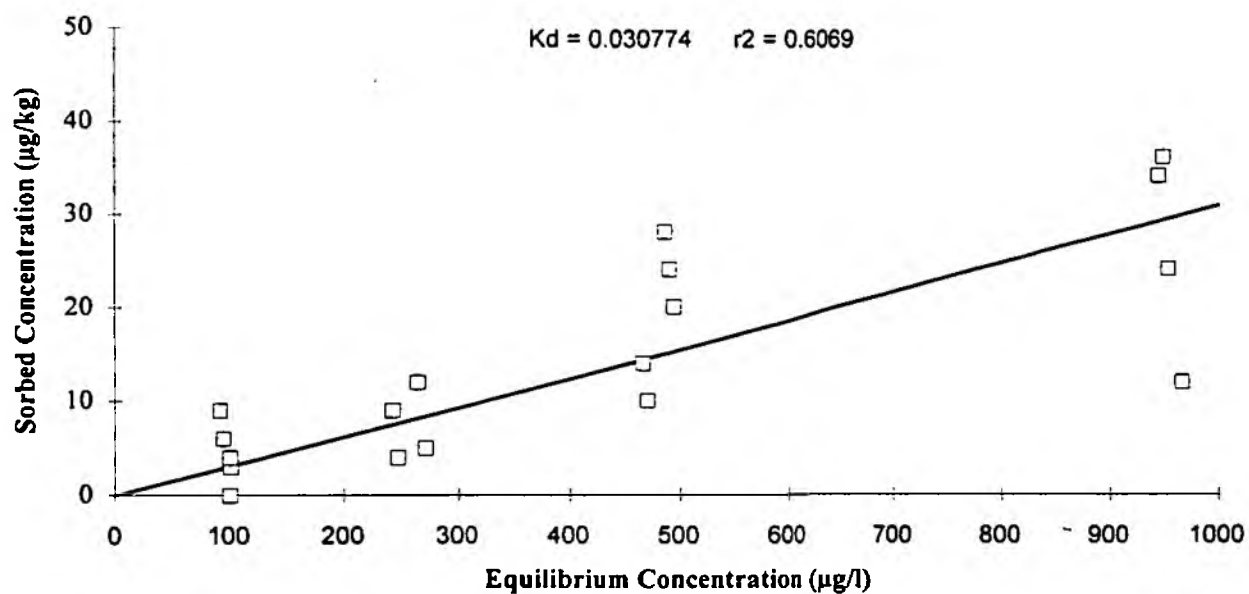


Figure A.1 Adsorption isotherm for atrazine to Upper Chalk

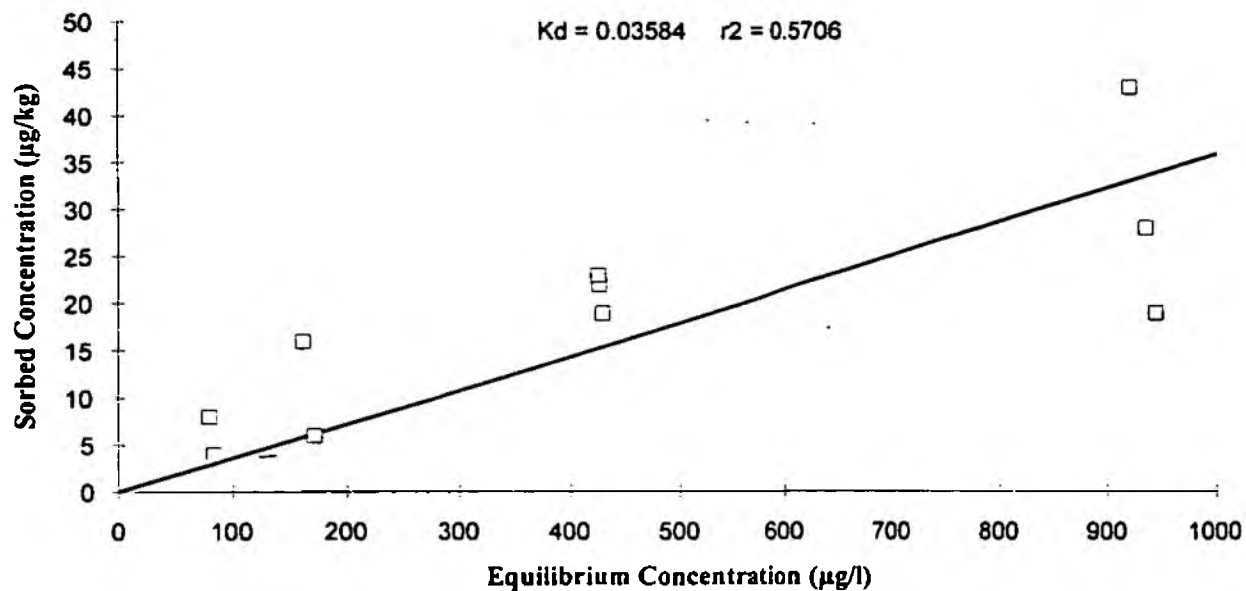


Figure A.2 Adsorption isotherm for atrazine to Middle Chalk

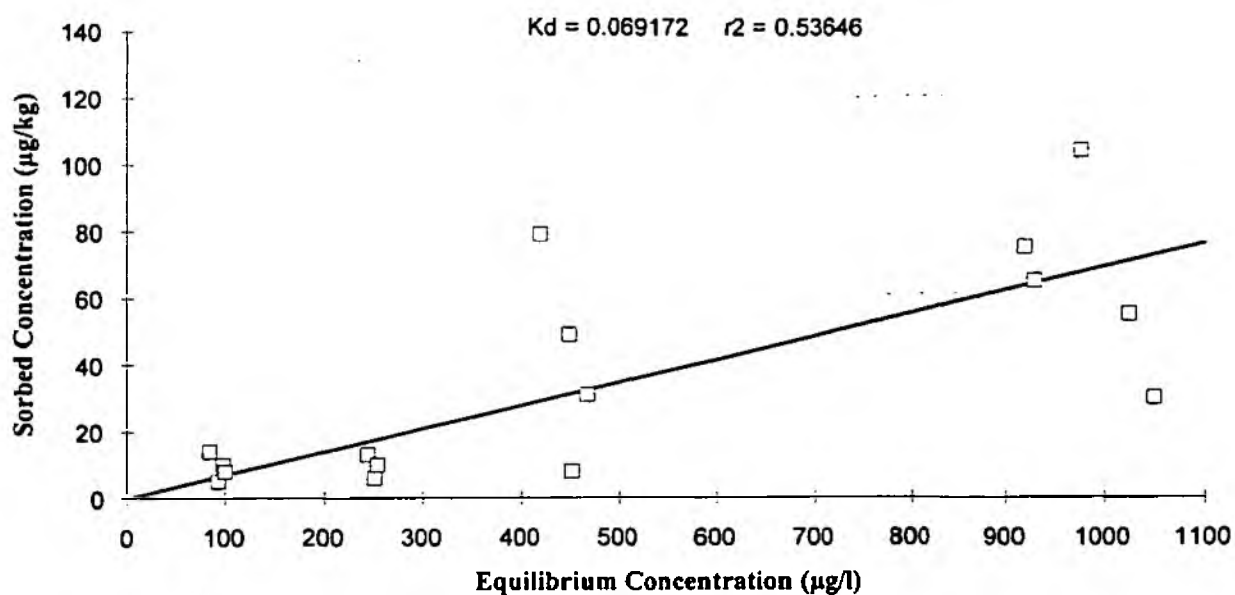


Figure A.3 Adsorption isotherm for atrazine to Lower Chalk

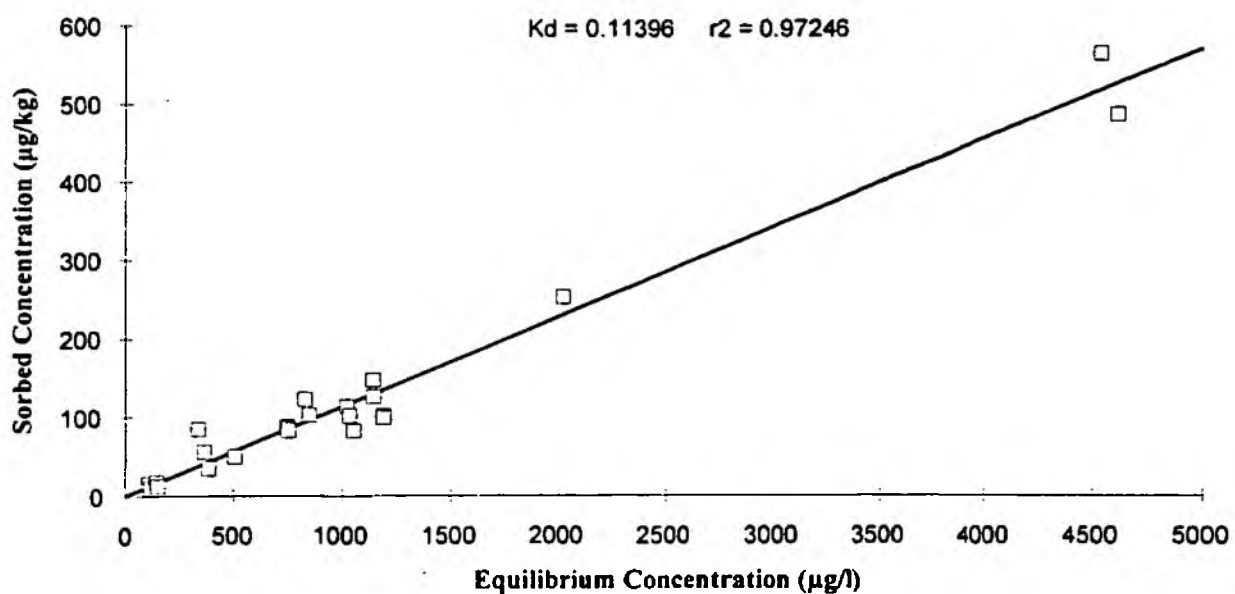


Figure A.4 Adsorption isotherm for atrazine to Putty Chalk

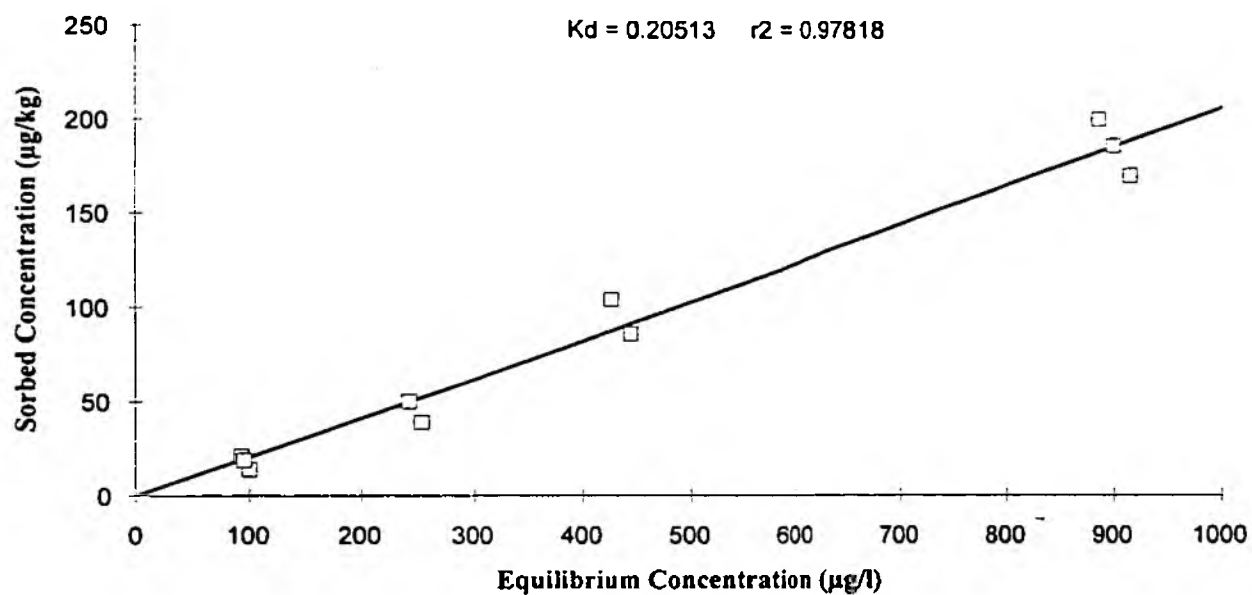


Figure A.5 Adsorption isotherm for atrazine to Marl Band

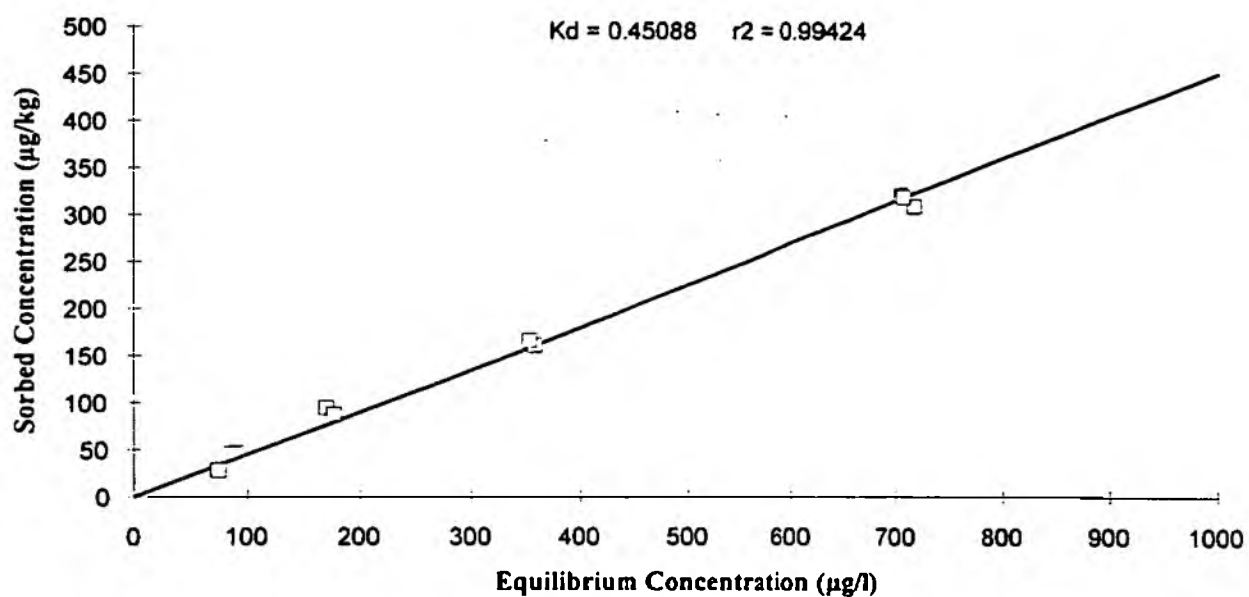


Figure A.6 Adsorption isotherm for atrazine to Soil

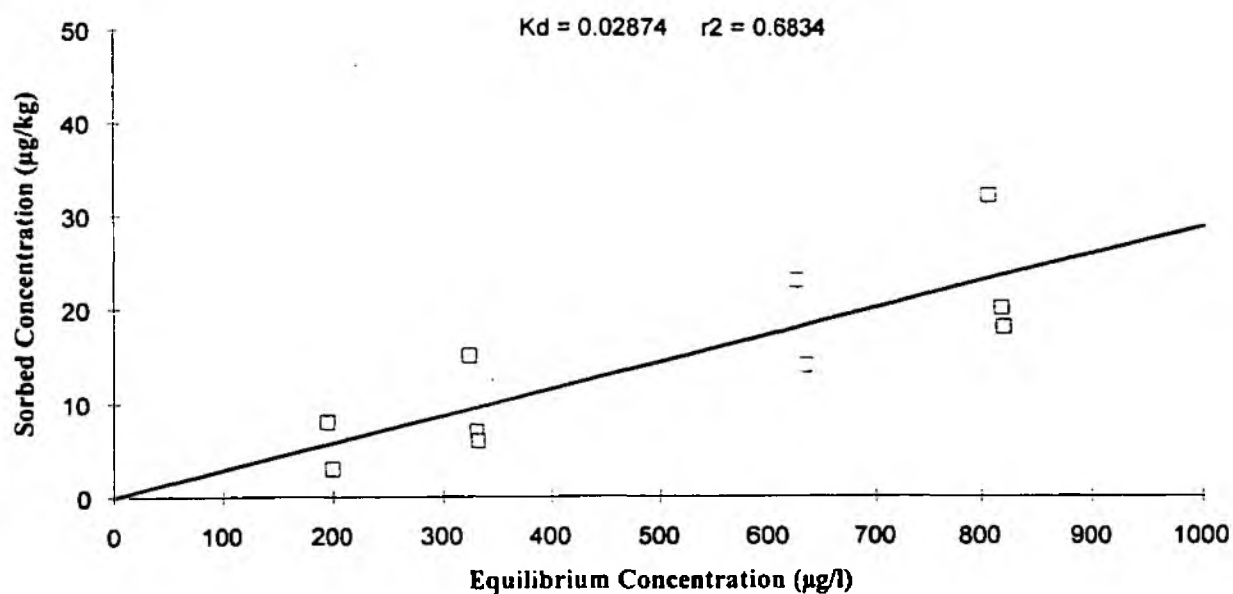


Figure A.7 Adsorption isotherm for simazine to Upper Chalk

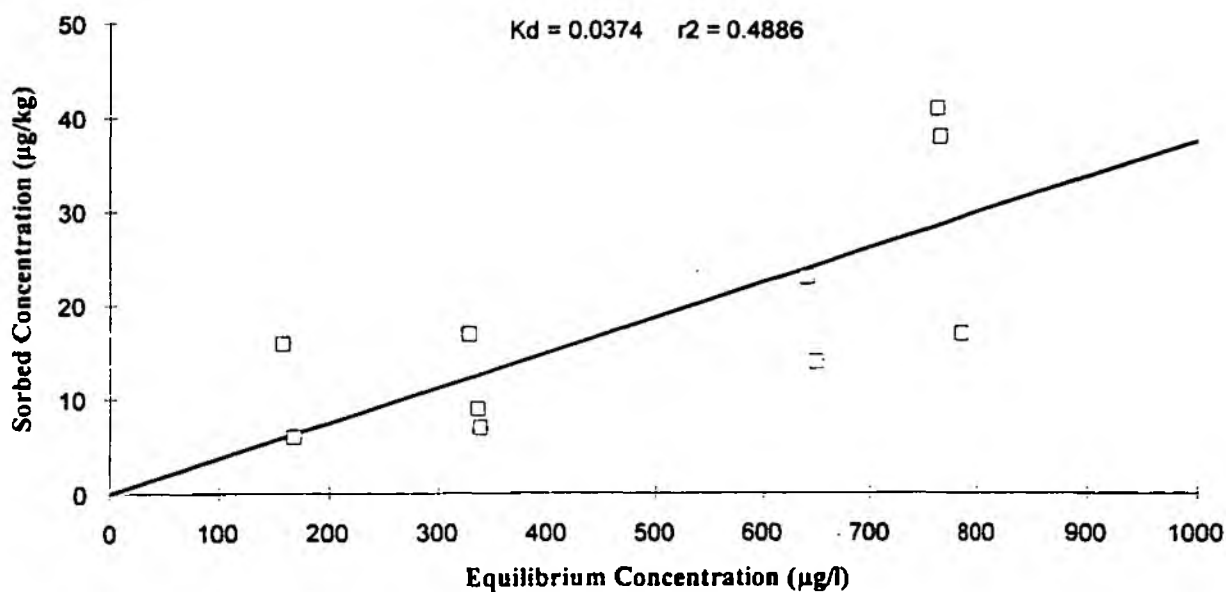


Figure A.8 Adsorption isotherm for simazine to Middle Chalk

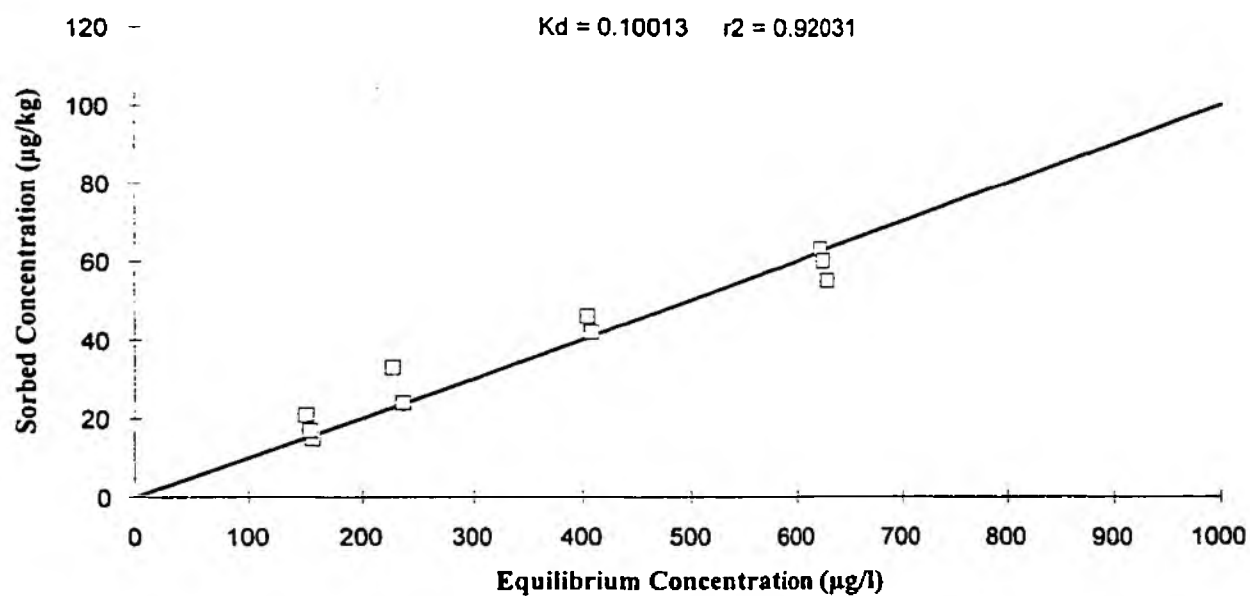


Figure A.9 Adsorption Isotherm for simazine to Lower Chalk

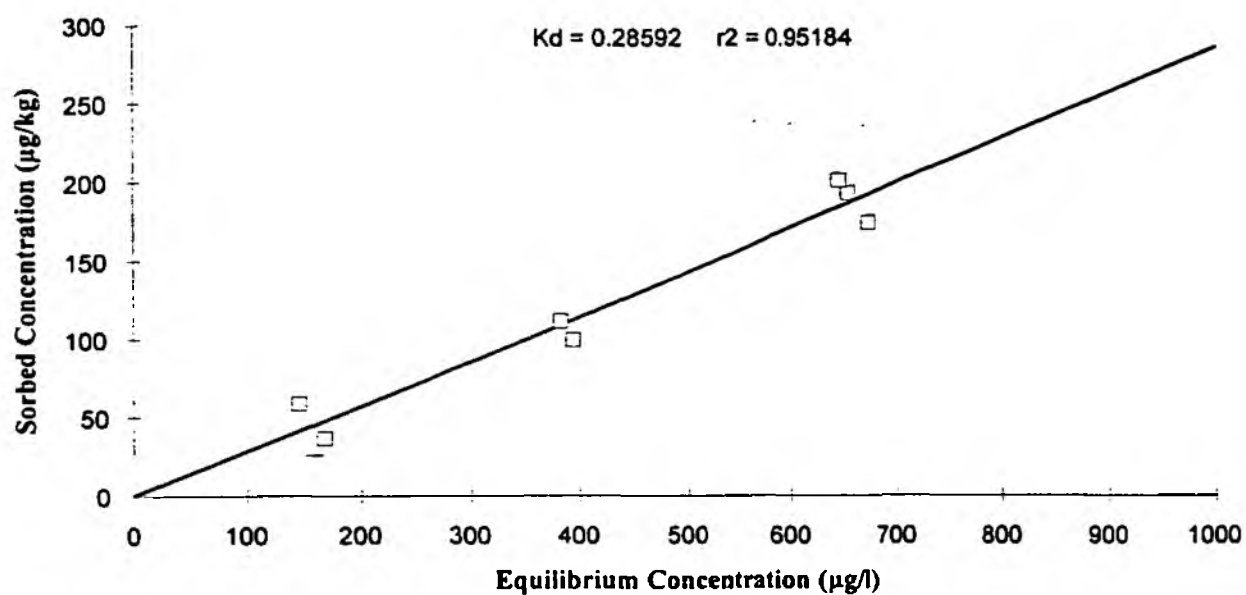


Figure A.10 Adsorption isotherm for simazine to Putty Chalk

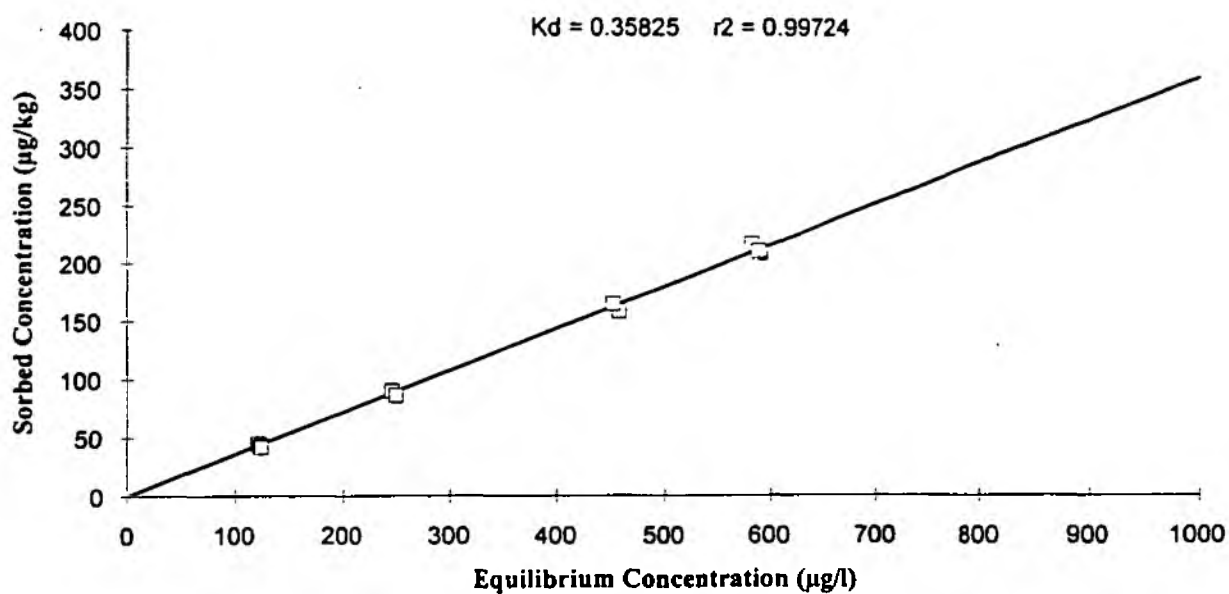


Figure A.11 Adsorption isotherm for simazine to Marl Band

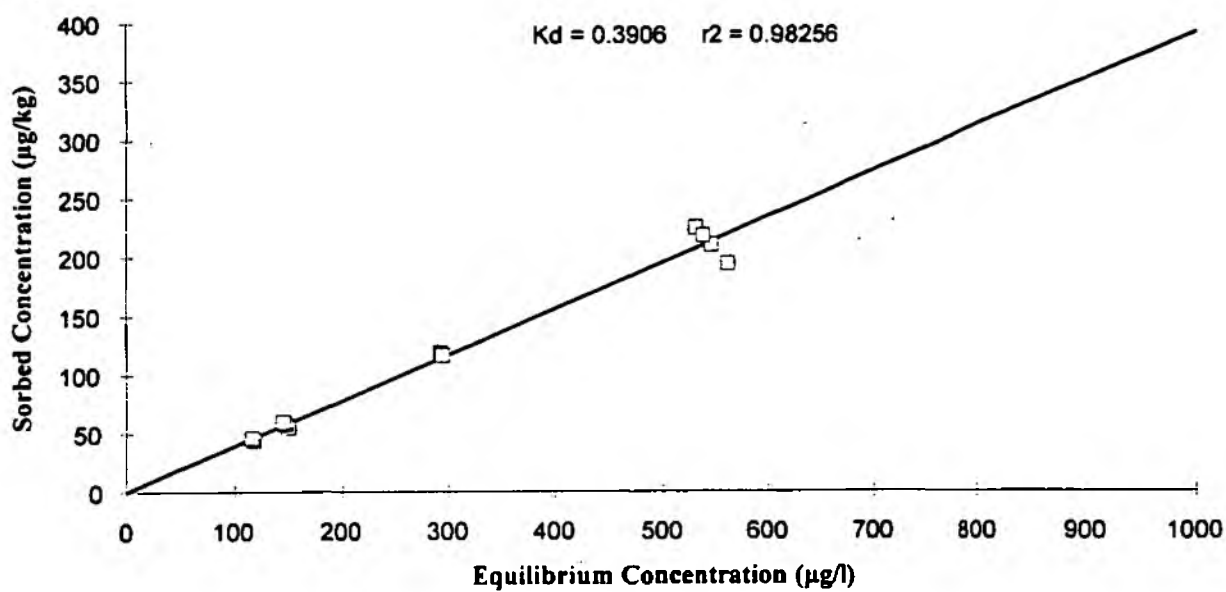


Figure A.12 Adsorption isotherm for simazine to Soil