Mechanisms of Groundwater Pollution by Pesticides

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ABSTRACT

An increasing number of pesticide compounds are being detected in groundwater supplies worldwide. There has, nevertheless, been little research into the mechanisms by which such pollution occurs and the routes via which pesticides move from the land surface into aquifers. In view of the potential time-lag in the response of groundwater systems to pollution inputs, such knowledge is essential if the current situation is to be appraised adequately and if any necessary controls on pesticide use are to be introduced.

From basic data on the physicochemical properties of pesticide compounds and on groundwater flow and pollutant transport in the principal British aquifers, some useful observations can be made about the relative significance of different mechanisms of potential groundwater pollution. These mechanisms and their implications for field research on pesticide pollution of groundwater are discussed. This problem is compared and contrasted to that of nitrate pollution from agricultural land-use practices.

Key words: Agricultural pollution; diffuse pollution; groundwater pollution; herbicides; pesticides; unsaturated zone.

INTRODUCTION

Background

During the past 10–15 years, much attention has been given to the leaching of nitrates from agricultural soils into groundwater, but the question of leaching pesticides is only just beginning to be addressed[1]. The use of pesticides has increased considerably since the 1960s and 1970s, and most rapidly in the case of herbicides and fungicides applied to winter-sown cereals. There has also been increasing non-agricultural use of triazine compounds for general defoliation, and unit rates of application for this purpose are believed to be much higher than in agricultural uses.

All pesticide compounds pose a significant environmental-health hazard since they are, to a greater or lesser degree, chemically-tailored to be toxic and persistent. The stringent EC Directive for maximum admissible concentration of pesticides in drinking water of 0.1 µg/l (effectively surrogate zero) has already been considerably exceeded in many British public water-supply boreholes[2,3], although concentrations in excess of 1 µg/l have seldom been recorded. The pesticides most frequently encountered to date are all herbicides – atrazine, simazine, mecoprop and isoproturon. The first of these, together with various soil insecticides, notably the carbamates and chloropropanes, have been found in concentrations exceeding 1 µg/l in shallow aquifers elsewhere in Europe and in the US[4,5,6,7,8].

Most groundwater systems are generally characterized by relatively slow rates of groundwater flow and pollutant transport. The average response period of deep water-supply boreholes in unconfined aquifers to surface inputs of (even mobile) pollutants is in the order of decades, as has been clearly demonstrated by diffuse nitrate pollution from soil-cultivation practices[3,9]. This slow response means that the analysis of pesticides (and other contaminants) from deep water-supply boreholes is an insensitive and tardy indicator of the state of quality deterioration in the groundwater system as a whole.

To appraise adequately the current situation and to justify any required controls, data are needed on the three-dimensional subsurface distribution of pesticide compounds beneath aquifer recharge areas, and especially in the unsaturated zone. Such investigation is presenting significant sampling and analytical problems and is likely to prove costly[1] because of:

- *(a)* The wide range of pesticide compounds in common agricultural use, many of which break down into toxic derivatives;
- *(b)* The need to work at very low concentrations because of the high toxicity of many of the compounds concerned, which necessitates the collection and handling of relatively large volume water and soil samples; and
- *(c)* The considerable care required to avoid sample modification by cross-contamination or volatile loss.

Scope

In view of the many difficulties and high costs involved with field investigation, an essential pre-

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requisite is to identify the most likely source of pesticide contamination and the most probable mechanisms of transport from the land surface to groundwater (Fig. 1). Such information is needed to specify investigation procedures, sampling protocols and monitoring networks, in order to rationalize investigation programmes.

Useful assessment can be made of the probable transport of pesticides into groundwater systems, based on the physicochemical properties of the pesticides themselves and on knowledge of groundwater flow and pollutant transport in British aquifers gained from earlier research.

It is the aim of this paper to make such an assessment as a guide to future field investigations and to address three fundamental questions:

- (i) Which pesticide compounds are most likely to be transported to groundwater?
- (ii) What are the most probable transport routes?
- (iii) Are the pesticide concentrations currently detected in water-supply boreholes likely to be approaching equilibrium with current pesticide application and leaching?

The local groundwater pollution risk from pesticide handling, veterinary use on farm animals, and disposal of unwanted compounds is beyond the scope of this paper.

Factors Affecting Leaching from Soil

Typical rates of agricultural pesticide application in the UK are in the range 0.2–5.0 kg/ha.annum of active ingredient. Much higher rates of pesticide application are common in essentially non-agricultural use for total defoliation. Such applications are used to eliminate all vegetation from railways, highways, airfields and other paved areas, forestry fire breaks and in fruit orchards.

Generally less than 10% of pesticide applications reaches the target area[10], and a significant portion remains for some time in the soil; this can be leached, either directly to groundwater or, in less permeable soils, via land drains to surface watercourses.

Most pesticide compounds have water solubilities in excess of 10 mg/l (10 000 μg/l), and this is not a limiting factor in leaching from soils. Of greatest importance in this respect is their mobility in soil solution. This will vary with affinity for organic matter and/or clay minerals, and can be expressed by the corresponding partition coefficient. This is normally only available for non-polar adsorption on organic carbon (K_{oc}) (Table I). An important anomaly in respect of subsurface pesticide mobility is the fact that some, otherwise strongly-adsorbed, compounds can be mobile in fissured or coarse-grained formations in the sorbed phase, if attached to colloidal particles[11].

Both the mode of application and action of the pesticide are important factors in relation to soil leaching, since those targeted at plant roots and soil insects are much more mobile than those acting through leaves.

Chemical reactivity of the compound with the soil matrix may also play an important role in reducing the risk of pesticide leaching, as a result of the generation of less soluble residues (Table I), for example through neutralization of acidic compounds in alkaline soils.

The degradability of pesticide compounds in the soil horizon, as a result of bacteriological oxidation or chemical hydrolysis, will often be significant. Soil half-lives for compounds currently in widespread use in the UK range from 10 days up to 10 years (Table I), but for the more mobile compounds are normally less than 100 days. However, in the UK many herbicides are applied pre-weed emergence, and some insecticides are used for soil treatment. Also, given the timing of these applications, they are sufficiently persistent to remain in the soil for

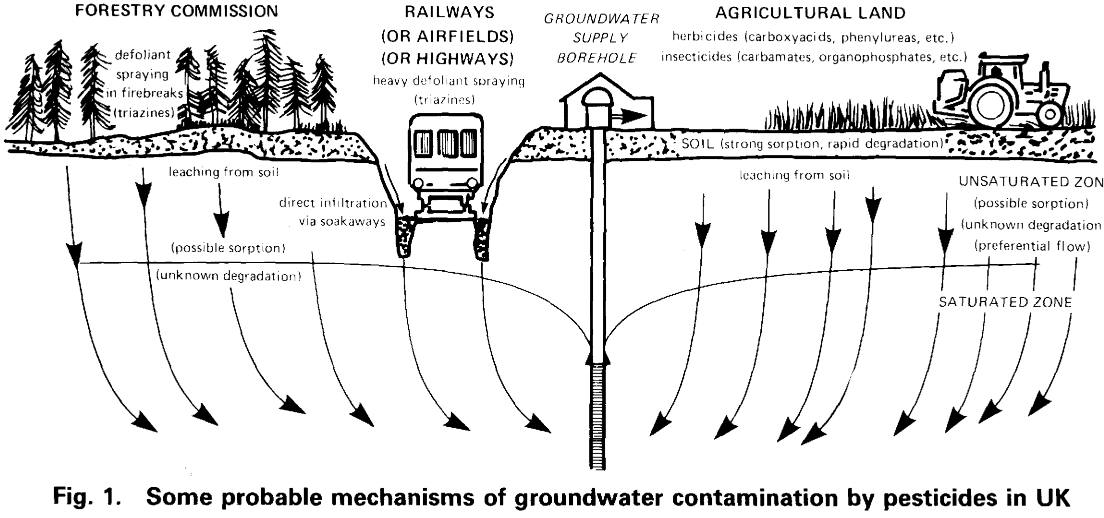

Fig. 1. Some probable mechanisms of groundwater contamination by pesticides in UK

TABLE I. SUMMARY OF PHYSICOCHEMICAL PROPERTIES OF PESTICIDES IN MAIN USAGE IN UK

Compound	Pesticide		Usage in UK* (T/a)	Partition coefficient* K_{oc} (mg/g)	Fertile soil half-life* (d)	Chemical behaviour
	Group	Type				
Isoproturon	Phenylurea	Herb–s	2000+	100–200	20–50	
Mecoprop	Carboxyacid	Herb–s	2000+	100–200	10–20	Acidic (may form insoluble Ca salts)
Chlorotoluron	Phenylurea	Herb–s	1000–2000	100–200	20–50	
Atrazine	Triazine	Herb–l	**	100–200	50–100	Basic (pH-related chemical hydrolysis important)
Simazine	Triazine	Herb–l	**	50–100	50–100	
Paraquat	Pyridine	Herb–l	200–500	>20,000	>2000	Cationic
Carbendazim	Triazole	Fung–l	200–500	n.a.	n.a.	
Aldicarb***	Carbamate	Ins–s	100–200	20–50	50–100	
Lindane***	Organochlorine	Ins–l	50–100	1000–2000	200–500	
Dimethoate***	Carbamate	Ins–s	<50	10–20	n.a.	
DBCP***	Chloropropane	Ins–s	<50	50–100	100–200	

*Order-of-magnitude ranges given because actual values vary considerably with data source.
**No total usage figures available; although relatively minor use in agriculture, non-agricultural use is believed to be considerable.
***Not in major use in UK, but included for comparison because cited frequently in international literature.
Herb = herbicide; Fung = fungicide; Ins = insecticide.
–s = soil or root-acting; –l = leaf acting.
n.a. = not available.

significant periods, when leaching may occur. Moreover, some derivatives of partial oxidation or hydrolysis may be equally toxic and/or mobile as the original pesticide compounds themselves.

It must be borne in mind that the adsorption and degradation characteristics of pesticides, listed in handbooks of chemical compounds in terms of partition coefficient and half-life (Table I), relate to a (standard) fertile organic clay soil. They will not be representative of (more permeable) sandy soils widely developed on aquifer outcrops, which are likely to be more vulnerable to pesticide leaching.

MECHANISMS OF TRANSPORT THROUGH UNSATURATED ZONE

FUNDAMENTAL CONSIDERATIONS

Pesticide compounds leached from permeable soils into the unsaturated zone enter an environment which contains a much smaller proportion of clay minerals and organic matter, and has a greatly reduced population of indigenous bacteria. Thus the mobility and persistence of all pesticide compounds should be expected to be many times greater in the unsaturated zone than in a typical agricultural soil[1,12]. No well-corroborated data are, as yet, available on the corresponding parameters for British aquifers.

The retardation in transport of chemicals experiencing adsorption, with respect to that of a conservative non-reactive mobile solute, can be estimated from their physicochemical characteristics using the expression:

$$R_t = \frac{1 + K_D \varrho_B}{n} \quad \ldots \quad \ldots \quad \ldots (1)$$

where R_t (the retardation factor) is the actual velocity of water flow divided by the transport velocity of the adsorbed species, and ϱ_B and n are the density and porosity of the porous media respectively. K_D (the partition coefficient) is the slope of the linear portion of the isotherm for adsorption onto organic matter, which can be approximately estimated from the corresponding coefficient for organic carbon (K_{oc}). An equation of this form was first applied to groundwater systems in 1959[13], and more rigorously proven in the early 1980s[14,15]. It strictly applies to one-dimensional saturated flow. When considering unsaturated zone transport, the equation can be re-expressed in terms of θ the moisture content, and ϱs the grain density of the porous matrix such that:

$$R_t = 1 + \frac{K_D(1 - n)\varrho s}{\theta} \quad \ldots \quad \ldots (2)$$

ORGANIC MATTER IN BRITISH AQUIFERS

The proportion of organic matter in most British aquifers is low (Table II), although organic carbon may be present in the aquifer matrix as a range of compounds. Not nearly enough is known about the precise specification of this carbon, but it will normally fall into three main groups:

(*a*) Fulvic and humic acids, which are immature polar material, generally similar to much soil organic matter. Adsorption from aqueous solution onto such materials is probably well represented by the equilibrium partition coefficient (K_{oc});

(*b*) Bitumens and related materials, which are of lower molecular weight, but more mature, less soluble and related to crude oils. Adsorption to these less polar materials would reduce for highly-substituted pesticide compounds, but should still be generally related to K_{oc}; and

TABLE II. Typical Ranges of Physicochemical Properties for British Aquifers

Aquifer	Grain density (ϱs) (g/cm^3)	Porosity (n)	Specific retention (Sr)*	Organic carbon content (% weight)
Chalk	2.72	0.30–0.45	0.29–0.43	0.05–0.2
Triassic Sandstone	2.65	0.20–0.30	0.12–0.18	0.02–0.05
Jurassic Limestone	2.72	0.10–0.25	0.08–0.22	0.2–2

*Corresponding to porosity range given and approximately equivalent to moisture content (θ) in unsaturated zone below zero flux plane

(*c*) Kerogen, which is a high molecular weight, insoluble organic material, having a graphitic character and unlikely to be very active in adsorption processes.

Amongst British aquifers, the Chalk contains (relatively) the largest amount of adsorbing species, which are disseminated widely within the matrix. The Jurassic Limestones contain the highest overall proportion of organic carbon, but this is unevenly distributed and may include a much higher percentage of kerogen-type materials. The Triassic Sandstones are believed to contain only low levels of mature refractory organic matter, consistent with their highly-oxidized characteristics.

Matrix Transport

Using available data on the physicochemical properties of British aquifers (Table II), estimates of R_t expected for matrix transport of pesticides of known K_{oc} can be made (Fig. 2), using equation (2).

It must be borne in mind that the derivation and application of this equation involves many assumptions:

(i) It strictly refers only to porous media that approximate to the uniform homogeneous ideal. The evidence of unsaturated zone profiles of environmental tritium suggest that some facies of the Chalk and Triassic Sandstone promote relatively uniform (non-dispersive) solute transport under natural rainfall conditions, although this uniformity is likely to result from interchange by aqueous molecular diffusion between mobile water in macropores/microfissures and much larger volumes of immobile water in the microporous matrix[16,17]. It is not yet known whether pesticides will have sufficiently high aqueous diffusion coefficients to enter into this process, although it is considered likely – at least for more mobile compounds;

(ii) In as much as K_D is calculated from the product of K_{oc} and the proportion of organic carbon in the porous media concerned, it is assumed that all organic matter present is equally active in pesticide adsorption, which for British aquifers has been noted to be unlikely;

(iii) By virtue of the fact that K_{oc} is determined from the linear portion of the adsorption isotherm, the equation assumes that adsorption processes are at equilibrium, which will only occur if water flow is sufficiently slow and sorbing materials are uniformly distributed throughout the porous media. In the case of pesticides, retardation due to adsorption on organic materials is normally the main process considered, although some compounds may also be sorbed by certain clay minerals; and

(iv) The transport of pesticides is assumed to be conservative, with no elimination due to biodegradation or chemical reaction.

While most of these assumptions will (to some degree) be violated in many cases, the approach gives an indication of the potential maximum retardation of pesticides in the unsaturated zone with respect to a mobile non-reactive solute. The matrix transport of such a solute is known to occur at natural rates normally in the range 0.5–1.5 m/annum in the unsaturated zone of British aquifers, from the evidence of profiles of environmental tritium. It is unlikely that matrix transport rates will exceed 1 m/annum except for the most mobile compounds. For many they would be much less than this value (Fig. 2). Since few compounds have been in regular widespread use for more than 10–20 years, most pesticides leached from agricultural soils would be expected still to remain in the unsaturated zone, except in areas of shallow groundwater table, if this was the only transport mechanism operative. Moreover, the rate of matrix transport would be highly sensitive to the proportion and the speciation of organic matter present in the porous media.

Preferential Flow

The hydraulic characteristics of most British aquifers are such as to present high probability of the development of so-called preferential (or bypass) flow in the unsaturated zone. This term is taken to include all forms of rapid downwater movement, in macropores and fissures (Fig. 3), effectively by-passing the matrix.

Preferential flow can be caused by numerous factors[18,19,20,21], and is often associated with instability of downward flow in situations where a permeable formation is overlain by a somewhat less permeable soil horizon[22].

In the case of British aquifers, the potential for preferential flow is immediately evident from their consolidated fractured character and the existence of high fissure hydraulic conductivity, which has been proven in the case of the Chalk at some sites[23,24].

Preferential flow is difficult to prove, especially under natural rainfall conditions. Because of the 'pressure to model' it has almost certainly been underestimated in past nitrate transport modelling of the unsaturated zone. Indirect evidence, how-

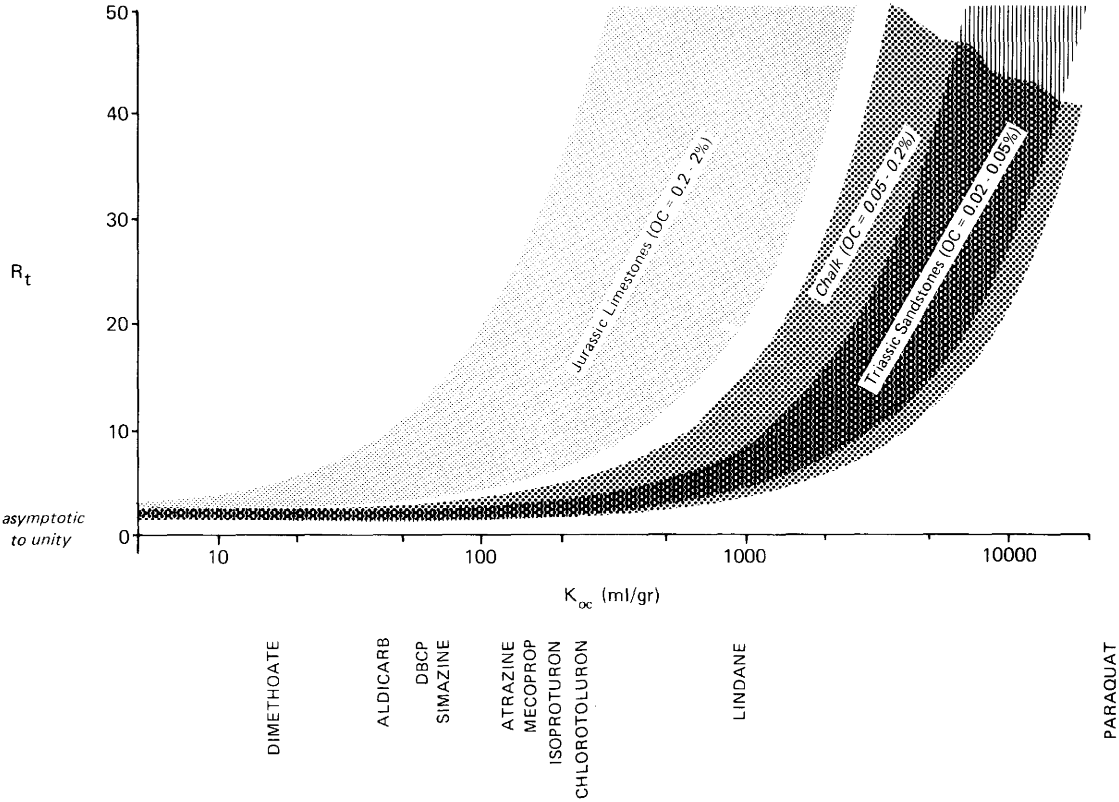

Fig. 2. Estimation of retardation factor for matrix transport of selected pesticides in British aquifers

ever, comes from the fact that many unsaturated zone matrix pore-water profiles of environmental tritium show marked dispersion with strong forward tailing of 1963–65 peak concentrations[25] (Fig. 4). This could only occur as a result of fissure flow in a dual-porosity system, when the velocity of water movement was high enough to prevent full interchange of solutes with the microporous matrix[17].

In areas where the hydraulic characteristics of the British aquifers have been investigated in considerable detail, and for which a reasonable number of unsaturated zone environmental tritium profiles are available, it is possible to make tentative estimates of the proportion of mobile solutes experiencing preferential flow in the unsaturated zone (Fig. 5).

Preferential flow is of major importance in the

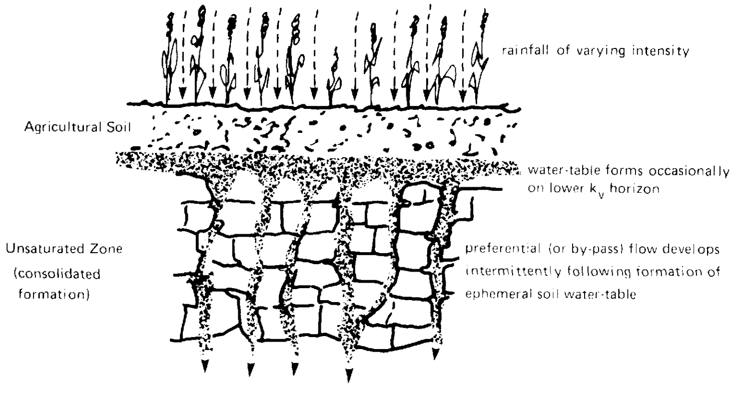

Fig. 3. Mechanism of development of preferential flow in the unsaturated zone of limestones and sandstones

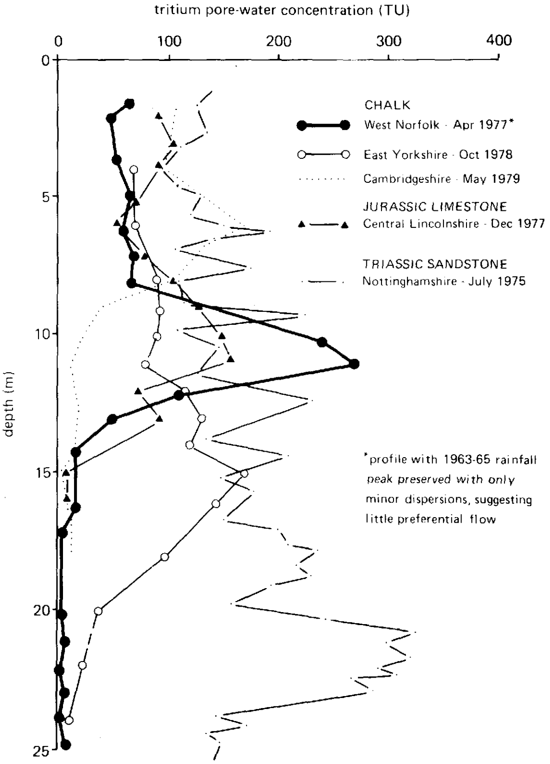

Fig. 4. Unsaturated zone profiles of environmental tritium providing evidence of preferential (dispersive) flow

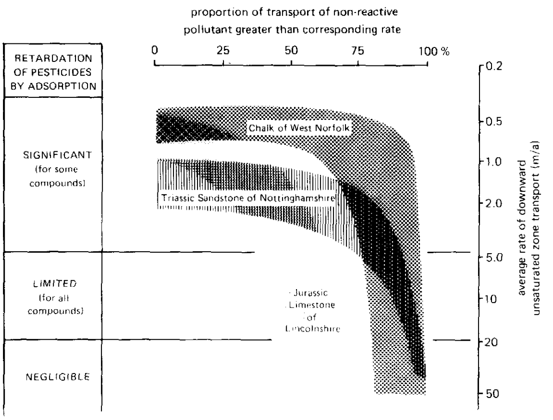

Fig. 5. Tentative estimate of rates of solute transport in unsaturated zone and relative significance of rapid preferential flow

consideration of pesticide transport into aquifers. Where developed, it would provide routes for deeper penetration of those pesticide compounds which are more readily leached from the soil by winter rainfall. Preferential flow would be characterized by much more rapid pollutant transport, providing less opportunity for retardation through molecular diffusion into the microporous matrix and associated adsorption, chemical reaction, and biodegradation. If preferential flow in fissures of larger aperture occurred, the possibility of transport of less mobile pesticide compounds adsorbed on colloidal material is also possible[11].

Preferential flow would be greatly favoured in situations where surface drainage to the ground was facilitated via soakaways (Fig. 1). Such a mechanism is probably responsible for the apparently widespread penetration of triazine compounds (atrazine and simazine), used as non-agricultural defoliants.

CONCLUDING DISCUSSION

Comparison of Pesticide and Nitrate Pollution Problems

The leaching of nitrate and pesticides from permeable agricultural soils and the associated groundwater contamination problems have many similarities. There are also important differences:

(*a*) The concentration of a soil-acting pesticide in soilwater solution required to achieve its agronomic objective is 1000s of times greater than the corresponding maximum EC guideline for drinking water. The equivalent ratio for nitrate is in the range 1.5–2.5;

(*b*) Highest soil-water nitrate concentrations occur in autumn, when matrix suction will also be high, whereas maximum soil-water herbicide concentrations are likely after spraying in late winter/early spring, when soils are likely to approach 'field-capacity' moisture content; and

(*c*) Transport of pesticides by preferential flow is thus more likely, and if it occurs will be more significant than for nitrates, because proportionally much higher concentrations are likely to be involved.

The extent of any unsaturated zone matrix transport of pesticides remains uncertain. This mechanism could produce an impact similar to that for nitrate, although even more delayed as a result of later initial inputs and retardation due to adsorption. Such a process may, however, be limited (at least for certain compounds) because of the much lower aqueous diffusion coefficients of pesticides and the possibility of their degradation by bacterial or chemical breakdown.

Whatever is the situation regarding unsaturated zone matrix transport, pesticide concentrations in water-supply boreholes are unlikely to approach equilibrium with current pesticide leaching for many years. This is because the large storage capacity of the saturated zone itself results initially in major dispersion and mixing.

INVESTIGATION AND MONITORING DIFFICULTIES

Pollution of groundwater by pesticides is a potentially-serious, and most certainly complex, environmental problem. It will require thorough investigation and careful monitoring to find a satisfactory solution and a reasonable balance of interests.

Field investigation and monitoring present formidable challenges. This is the result of a number of factors:

(i) A substantial number of pesticide compounds, together with their many toxic derivatives, may be involved – even within a relatively limited geographic area. New compounds are frequently introduced, but many do not stay in use for a long period of time. For example, individual arable fields on the Chalk outcrop are likely to receive 4–5 applications per year involving 2 or 3 different compounds. As a result, such fields may have received applications of 10–20 separate compounds in a 10-year period, the intention being to reduce the likelihood of developing weed/pest resistance and to avoid carry-over problems in subsequent sensitive crops. This greatly complicates investigation of the environmental distribution of pesticide compounds and the determination of the total pesticides in water-supplies, an important issue given that the EC state a guideline value in this respect (0.5 μg/l), as well as for individual compounds;

(ii) Profiling pesticide concentrations in matrix pore-water is difficult because of the problem of obtaining and extracting adequate sample volumes to reach an analytical detection limit of even 1 μg/l. It can only realistically be attempted at experimental agricultural plots, where trials of individual pesticides have been, or are being, conducted. At an experimental cereal-growing site on the Berkshire Chalk, at which only the herbicides Mecoprop and Paraquat had been used on a regular basis, pore-water samples were obtained from a depth of 0.6–3.4 m by centrifugation of Chalk blocks obtained from trenches. Both Mecroprop and Paraquat were below their respective detection limits of 0.5 and 5.0 μg/l respectively, given the sampling method employed; and

(iii) Sampling of preferential flow beneath permeable soils is even more difficult, especially bearing in mind its limited duration following heavy rainfall. One option would be to install large-scale lysimeters at experimental sites, but it is probably more realistic to concentrate upon pumped samples from monitoring piezometers set at the base of the zone of seasonal fluctuation in areas of shallow water-table.

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