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**REVIEW OF STRATEGIES FOR MODELLING
THE ENVIRONMENTAL FATE OF PESTICIDES DISCHARGED INTO RIVERINE SYSTEMS**

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ABSTRACT

Pesticides are often produced and stored in large quantities near rivers posing a potential hazard for the aquatic environment. Accidental incidents such as storage facility fires are of major concern as significant amounts of pesticide chemicals can enter the nearby riverine system possibly causing considerable environmental damage (for example the Sandoz fire in Basel in 1986 which polluted the Rhine river). In order to assess the potential impact on the riverine environment of such an incident it is necessary to identify the controlling environmental fate processes that affect pesticides in freshwater systems. A strategy for mathematically modelling these processes to predict the fate of the chemical contaminants then needs to be established. This paper discuss and reviews the major environmental controlling fate processes of selected herbicides in freshwater. Strategies on how to mathematical model the environmental fate of pesticides in rivers are also considered.

1. INTRODUCTION

Pesticides are introduced in aquatic environment through intentional application (control of aquatic weeds, algae, fish, or unwanted invertebrates), aerial drift, runoff from agricultural applications or runoff from accidental release. Accidents involving fires of pesticide storage or factories situated near rivers or estuaries have proved to be of particular concern. A well known example is the Sandoz accident that occurred in Basel in 1986, where 1350 tons of chemicals were combusted, and between 10000 and 15000 m³ of contaminated fire-fighting water were discharged into the Rhine river. Many of those chemicals were pesticides, and the impact on the environment was catastrophic (Capel et al., 1988).

As mentioned above it is common to find pesticide factories located near rivers or estuaries in European countries. Figure 1 shows the location of major pesticide plants within the UK mainland. The rivers form complex ecological systems in the natural environment, as illustrated in Figure 2. Rivers are directly linked to estuaries, coasts, and open seas where the pollutants are transported by the flow, and are in permanent contact with the atmosphere to which pollutants can be transferred through volatilization. The river system is also connected to the groundwater either because the groundwater feeds the river when the piezometrical level of the groundwater is higher than the level of water in the river, or because the river feeds the groundwater when the level of water in the river is higher than the piezometrical level of the groundwater. In the second case, the pollutants present in the river are transported into the groundwater and which may pollute both the ground and the drinking water. The pesticides present in the water can also pollute directly the surrounding land by adsorption through the groundwater or by the rain after volatilization into the atmosphere. Concern thus arises because of the location of many of the factories, the storage plants and the risk they potentially pose to the aquatic environment after an accidental fire.

Although numerous studies of fate of pesticides have been conducted relatively few deal with their fate in water (see for example Crossland *et al.* 1986). Moreover, these studies usually evaluate the ecological impact of *pure* products, not of mixtures of pesticides.

Herbicides form a major group of pesticides and in France, United Kingdom, and Denmark, they represent more than 50% of the production of pesticides every year. Such products enter the aquatic environment through the soil, directly when they are used to control the development of plants in rivers, or when an accident occurs in a storage plant and thus represent a potential threat to the aquatic environment.

The work presented in this paper is part of an overall programme to investigate the ecological impact on freshwater systems of pesticide warehouse fires. This paper reviews and discusses the role of the major fate processes of herbicides in water. The discussions focus on three herbicides; glyphosate, diquat and paraquat. Mathematical models to simulate and predict the fate processes of pesticides are also discussed in relation to pesticide storehouse fires. A possible strategy for mathematically modelling these fate processes is suggested.

2. FATE PROCESSES OF SELECTED HERBICIDES

Once pesticides enter the water environment they are subject to various physical, chemical and microbiological fate processes. Figure 3 shows the major fate processes effecting

pesticides in water and thus illustrates the complex nature of task to trying to understand such processes. This paper focuses on three herbicides that are widely used in Europe whose properties are summarised in Table 1. The choice of these herbicide was determined primarily by the fact that they degraded predominantly by defined fate processes. Glyphosate is primarily biodegraded, diquat and paraquat are photodecomposed, adsorbed, and biodegraded.

Glyphosate [N-(Phosphonomethyl)glycine] is a non selective organophosphorus aquatic herbicide, slightly toxic to aquatic fauna (Table 1), also used for vegetation control in forestry (Ghassemi & Quinlivan, 1982 ; Hutson & Roberts, 1987). It is an organophosphorus compound which possesses a carbon-phosphorus (C-P) bond. This C-P bond is resistant to chemical hydrolysis, thermal decomposition, and photolysis (Moore *et al.*, 1983). On the other hand, glyphosate is biodegraded by bacteria and adsorbed to clay.

Diquat [Dipyrido (1,2-a:2',1'-c)pyrazinediium,6,7,-dihydro-, dibromide monohydrate] and paraquat (4,4'-bipyridinium,1,1'-dimethyl-, dichloride) are pyridine herbicides. Both are more toxic to aquatic animals and invertebrates than glyphosate (Table 1). Diquat is used for aquatic weed control, potato haulm, and seed crop desiccation. Paraquat is used to clean the stubble, for inter-row weed control, crop desiccation, and elimination of old swards (Hutson & Roberts, 1987). Diquat and paraquat are degraded by photolysis, biodegradation, and are strongly adsorbed to clay.

2.1. Sorption

Sorption is a physicochemical dynamic process of pesticide-sediment-water interactions, correlated with the nature of the solids in the system (particle size distribution, type of clay mineral, clay content, organic matter content, cation exchange capacity) and the characteristics of the pesticide (water solubility, octanol-water partition coefficient, fugacity). The ability of a pesticide to be adsorbed on sediments depends on its polarity; a pesticide is adsorbed more when its polarity is low (Hutson & Roberts, 1990).

There are two sorption coefficients to evaluate the rate of sorption of a pesticide: (1) K_d the sorption partition coefficient, used for low concentrations of pesticide (K_d is expressed in l/kg):

$$K_d = \frac{\text{concentration in sediment}}{\text{concentration in water}}$$

and (2) K_{oc} , the adsorption coefficient, defined as the K_d corrected for the organic content of the sediment :

$$K_{oc} = \frac{K_d}{(\% \text{ organic carbon})} \times 100$$

The higher K_d and K_{oc} are, the greater the role of sorption assumes in the removal of the herbicide from the water (Reinert & Rodgers, 1987).

Once they are adsorbed to sediment, pesticides can be desorbed and be submitted to

subsequent diffusion in the river. The effect of adsorption-desorption on transport of pesticides in rivers is to retard their solute diffusion. The process of adsorption-desorption has been studied by Corwin and Farmer (1984) on the base of numerical models from Freundlich and Langmuir. These authors showed that in the case of strongly adsorbed cationic pesticides such as diquat and paraquat, the adsorbed phase degradation rate may be more significant than the degradation rate of pesticide in solution. A sediment with a high adsorptive capacity and a high strength of adsorption would release pesticide to the water at a slow rate and in low amounts, presenting less hazard of toxicology for aquatic organisms but a higher threat to filter-feeding organisms which rely upon organic matter at the sediment-water interface as a food source.

Glyphosate is readily adsorbed onto clay. Its adsorption increases when the pH of the clay-glyphosate system decreases. Glyphosate is also strongly adsorbed to Al^{3+} and Fe^{3+} , and is not adsorbed to Na^+ (Sprankle *et al.*, 1975; Grossbard & Atkinson, 1985; Mc Connell & Hossner, 1985). The consequence of this adsorption is that glyphosate is inactivated in soils that contain clay (Hance, 1976; Grossbard & Atkinson, 1985). Hartman and Martin (1984) studied the effect of suspended bentonite clay on acute toxicity (0 - 100 mg/l) of the herbicide glyphosate. The acute toxicity tests have been made on an aquatic invertebrate (*Daphnia pulex*) and an aquatic plant (*Lemna minor*). Other experiments have been conducted on glyphosate-sediment interactions and phytotoxicity on safflower roots in turbid water for low concentrations of glyphosate (< 6 mg/l) (Bowmer *et al.*, 1986). All these experiments showed that the effect of glyphosate adsorption to suspended clay on its toxicity depends on the way how the organisms utilise the media where they grow, and that the adsorption of glyphosate to clay is negligible for low concentration of the herbicide in water. For example, glyphosate gets unavailable to *Lemna minor*, a plant that removes dissolved constituents from the aqueous phase of the medium in which it grows, when there is no apparent lasting effect on *Daphnia pulex*, which ingests glyphosate with particulate matter by the filter-feeding.

Diquat and paraquat, because of their cationic properties, are strongly adsorbed to sediments and suspended materials, especially to clays that have a high cation-exchange capacity. The adsorption of these herbicides depends on the surface charge density of the clay and increases when pH decreases, but seems to be independent of the temperature and of the water solubility (Gunther & Gunther, 1970). As paraquat and diquat are very strongly adsorbed to soils and sediments, they are biologically unavailable in that form, reducing their rate of degradation by microorganisms (Eisler, 1990). Addition of clay on soil also decreases diquat and paraquat phytotoxicity because, after adsorption on the clay, the herbicide was less available for plant roots (Gunther & Gunther, 1970).

2.2. Photolysis

Much of the energy required to drive the environmental transformations of organic compounds comes directly from the solar radiation. Pesticides, dissolved or suspended in water or in gaseous phase, can absorb light and decompose spontaneously or by reaction with reagents generated by light (e.g. oxygen or ozone). Pesticide photodegradation, or photolysis, depends on different factors such as light quality and quantity, water turbidity, and pH (Hill & Wright, 1978).

The overall rate of pesticide photolysis can be expressed as follows (Schnoor, 1992) :

$$\frac{Dc}{dt} = -k_p C$$

with :

C = dissolved pesticide concentration
 $\frac{dC}{dt}$ = rate of photolysis
 k_p = photolysis rate constant
 t = time

The photolysis rate constant, k_p , is can be calculated with the following first order equation :

$$k_p = \frac{2.303}{J} f S I_l e_l$$

with :

k_p = photolysis rate constant
 J = conversion constant = $6.02 \cdot 10^{20}$
 f = quantum yield
 I_l = sunlight intensity at wavelength l
 e_l = molar absorptivity or molar extinction coefficient at wavelength l

There are two photochemical processes : (1) direct photolysis of pesticides proceeds via direct absorption of sunlight energy causing chemical reactions (its kinetics are composed of two factors ; light absorption and quantum yield), (2) indirect photolysis which requires a sensitizer to initiate light absorption (sensitizer include O_3).

UV light rapidly degrades both diquat and paraquat : 50% of the ^{14}C from both compounds is lost after 48 hours, and more than 75% is lost after 96 hours of exposure to UV light (Kearney & Kaufman, 1969 ; Reinert & Rodgers, 1987). Kearney and Kaufman proposed that the first compound of degradation of paraquat could be 1-methyl-4-carboxypyridinium ion. This compound could then be transformed to methylamine hydrochloride. It has been shown experimentally that paraquat can be photodegraded in soils by UV radiation in the presence of oxygen or ozone with 1-methyl-4-carboxypyridinium ion, 4-picolinic acid, hydroxy-4-picolinic acid, N-formylglycine, malic acid, and oxalic acid as reaction products (Eisler, 1990). Glyphosate on the other hand is stable to photolysis.

2.3. Biological transformation processes

Pesticides in the aquatic environment are taken up by organisms. The biota deals with pesticides in four different ways: (1) pesticides are accumulated in the body, eventually having a toxic effect on the organism or causing the death : this is bioconcentration or bioaccumulation, (2) they are transmitted to other organisms through the food chain and are accumulated by different organisms, particularly consumers at the upper end of the foodchain (e.g. birds of prey and man) : this is biomagnification, (3) they are transformed by organisms and excreted : this is biotransformation and is known to occur in some aquatic animals and even fungi, (4) they are decomposed significantly possibly even to mineral products such as CO_2 , CH_4 and H_2O : this is biodegradation and is .

Bioconcentration can be evaluated by two factors :

(1) the bioconcentration factor (BCF), that determines the potential of a compound to bioconcentrate within an organism, is defined as follows:

$$BCF = \frac{\text{concentration in living tissue}}{\text{concentration in water}}$$

the higher the BCF , the greater the potential for bioconcentration and long-term harm to aquatic organisms and aquatic environments (Reinert & Rodgers, 1987).

(2) the octanol-water partition coefficient (K_{ow}) measures the ease of the transfer of a chemical from the aqueous to the lipid phase. It is inversely proportional to the water solubility (W_s) of the herbicide (Mackay, 1980 ; Hutson & Roberts, 1990). K_{ow} is defined by the following equation :

$$K_{ow} = \frac{\text{concentration in octanol}}{\text{concentration in water}}$$

the larger the K_{ow} is, the higher is the rate of bioconcentration of the herbicide (Reinert & Rodgers, 1987). However, none of the selected herbicides is concentrated in biota.

Biotransformation occurs when the original compound is modified by organisms usually to reduce its toxicity. Biodegradation is the breakdown of a compound by microorganisms (HMSO, 1981). This may be : (1) primary (the alteration of the chemical structure of a substance resulting in loss of specific property of that substance) or (2) ultimate (the complete breakdown of a compound to either fully oxidised or reduced, simple molecules (e.g. CO_2 , CH_4 , H_2O , NO_3^- , NH_4^+) and the formation of new cells).

The total decay rate coefficient (K_T) can be calculated, if the degradation is first order, for each herbicide by adding the K values (K_{oc} , K_d , K_{ow}). Then, the half-life time ($t_{1/2}$) can be calculated as follows (Reinert & Rodgers, 1987) :

$$t_{1/2} = \frac{0.693}{K_T}$$

Herbicides with small K_T values will persist longer in the aquatic environment (large $t_{1/2}$) than herbicides with larger K_T (Reinert & Rodgers, 1987). The results obtained by this model should be verified experimentally.

Glyphosate is completely degraded in soil by micro-organisms. One of the major metabolites of this degradation is aminomethylphosphonic acid which is non toxic and also degraded in soils but at a slower rate than glyphosate (Rueppel *et al.*, 1977). Glyphosate decomposition has been shown under both aerobic and anaerobic conditions. This decomposition is closely correlated with microbial activity in soil (Muller *et al.*, 1981). Many bacteria, such as *Pseudomonas sp.* strain PG 2982 or *Flavobacterium sp.* strain GD1, utilising glyphosate as a sole phosphorus source have been isolated by different authors (Moore *et al.*, 1983 ; Shinabarger *et al.*, 1984 ; Balthazor & Hallas, 1986 ; Hallas *et al.*, 1988). Hallas *et al.* (1988) identified a total of 393 microbial strains showing a glyphosate-degradation activity, grouped in 81 generic clusters.

Biodegradation of glyphosate has been studied in industrial activated sludge (Balthazor & Hallas, 1986 ; Hallas *et al.*, 1988; Hallas *et al.*, 1992). It has been shown that glyphosate is first transformed to aminomethylphosphonic acid (AMPA) by cleavage with production of CO_2 , and AMPA is then mineralized by phosphonate activity that cleaves C-P bond to PO_4^{3-} , with production of NH_4^+ , CO_2 and H_2O .

Numerous aerobic and anaerobic organisms (e.g., *Corynebacterium fascians*, *Clostridium pasteurianum*, *C. fascians*, *Lipomyces starkeyi*) can use paraquat and diquat as a sole source of carbon or nitrogen (Kearney & Kaufman, 1969). Actinomycetes, including species of *Streptomyces* and *Nocardia*, have also been shown to degrade paraquat forming 1-methyl-4-carboxypyridinium ion (Hill and Wright, 1978). The formation of 1-methyl-4-carboxypyridinium ion (N-methylisonicotinic acid) was first proposed as the product of paraquat biodegradation by an unidentified bacterium in 1967 (Hill and Wright, 1978). The

proposed pathway of degradation was in two steps : (1) initial demethylation that transforms paraquat into 1-methyl-4,4'-dipyridinium ion, and (2) cleavage of one of the pyridine rings that transforms 1-methyl-4,4'-dipyridinium ion into 1-methyl-4-carboxypyridinium ion.

3. MATHEMATICAL MODELLING STRATEGIES

3.1 Mathematical Models

A common way to model the transport of pesticides in rivers is based on compartmentalization of the river in sections (Neely *et al.*, 1976 ; Chen, 1979 ; Thomas, 1979 ; Yoshida *et al.*, 1983 ; Schnoor *et al.*, 1987). Modelling of transport can often be simplified by making the assumptions that the bed stream is uniform, and that the velocity and density of sediment are constant. As these assumptions can be justified only over a short length of the river and it is necessary to model the stream in sections. The transport of pollutants and sediments can then be calculated in each section and aggregated to obtain the transport characteristics through the whole river.

Biodegradation of pesticides in soil has been modelled by Soulas (1981), taking into account four populations of micro-organisms: (1) metabolizing micro-organisms which degrade the pesticide and use it as a source of nutrient ; (2) co-metabolism micro-organisms which degrade or transform the pesticide without using it as a source of nutrient ; (3) non-degrading sensitive micro-organisms which are sensitive to the lethal action of the chemical ; and (4) non-degrading non-sensitive micro-organisms which are indifferent to the lethal action of the chemical. On the other hand, biodegradation of pesticides in water has not been studied or modelled in detail.

The strategy for modelling adsorption and desorption processes employed by Corwin and Farmer (1984) has been tested on diquat and has shown that this herbicide is strongly adsorbed to clay and that its rate of desorption was very low. Direct photolysis has been modelled by Zepp and Cline (1977) under the assumption that the pollutant is isotropically distributed in the water body and the amount of light is constant during a given period of time. These assumptions can be verified if the river is treated in sections along the length of the bed of the river and in subsections along the depth of the river where the rate of light decreases. Crossland *et al* (1986) used the mathematical model SOLAR to predict the rate of phototransformation of pentachlorophenol and dichloroaniline in ponds. This model was based on the following parameters: light absorbance of the pond water, its depth, the season, and the latitude.

A range of aquatic chemical fate models have been reviewed in Samiullah (1990). In particular the application of fugacity models to study environmental partitioning have been discussed. A feature of fugacity modelling is that they can be applied at various complexity levels (Mackay *et al* 1983). Such a model employs a compartmental approach where each compartment is a volume in which the chemical is in a selected environment and is subject to selected processes. The chemical is assumed to move from one compartment to another according to the laws of chemical kinetics.

3.2. Discussion on Mathematical Modelling Strategies

When a pesticide spill occurs into a river it is important to model the transport and the fate of pesticides along the whole stream so that a complete assessment of the ecological impact can be made. The relative contributions of the major interacting fate process have to be taken into account by the adopted modelling strategy. The previous section

described mathematical models that compute the transport and the fate processes of the selected herbicides in water. as there are many complicated biogeochemical processes taking place it is usual to make simplifying assumptions. Such as, parameters such as velocity, light, or concentration of sediments may have to be assumed to be constant over a specific section of the river. As these assumptions can be justified only over in a limited space and time period it may be necessary to treat the river in sections of length and subsections of depth. The transport and the fate processes can then be modelled in each section. Whichever strategy is adopted it has to be formulated in light of the overall objectives set for the model. These may include:

- (1) How fast will the pesticides be degraded in the river ?
- (2) Where and how fast will the pesticides be transported in the river ?
- (3) What concentrations will the pesticides attain in each riverine compartment?
- (4) What implications do these levels have in terms of ecotoxicity ?

The first stage involves deciding which are the most important fate processes. For example, in the case of degradation of glyphosate, two major fate processes are involved ; biodegradation and sorption. Biodegradation and adsorption to clay in benthic sediment or on suspended sediment have negative influences on each other. The more glyphosate is degraded, the less it will be adsorbed to clay, however the more it is adsorbed, the less it is available for microorganisms and hence it will be less biodegraded. The process is opposite with desorption. Biodegradation increases with desorption because as glyphosate becomes available for microorganisms. The situation is similar with diquat and paraquat except that these herbicides are very rapidly degraded by photolysis. Biodegradation and photolysis may have negative influences on each other, although the product of photolysis may well be biodegradable.

In the second stage the influence of the fate processes on transport has to be ascertained, that is, whether they increase the rate of transport or decrease it. Cases of glyphosate, diquat and paraquat are similar, the degradation processes (biodegradation for glyphosate, photolysis and biodegradation for diquat and paraquat) decrease the quantity of the parent pesticide transported along the river. Adsorption to clay in benthic sediment also decreases the rate of transport. Adsorption to suspended solids and desorption would tend to increase the rate of transport.

As an example the multiple pathways that can result of the different fate interactions are illustrated in the case of glyphosate, see Figure 4. It is convenient to consider the quantity of product degraded and that adsorbed and how the fate processes affects the transport of the pesticides through the river. When glyphosate enters the river, a certain quantity (Q_b) will be directly biodegraded. This quantity is equal to the total amount of pesticide discharged into the river (Q_t) minus the quantity adsorbed to benthic sediment (Q_a) and to suspended sediment (Q_s). During the time it takes to be degraded it, glyphosate will be transported along the river (time T_b). With regard to the amount of glyphosate adsorbed onto clay particles, glyphosate can either be desorbed and biodegraded (quantity Q_{ad} and Q_{sd}) or directly biodegraded (quantity Q_{ab} and Q_{sb}). If glyphosate is adsorbed to clay in benthic sediment and then directly biodegraded, it will not be transported ; if it is then desorbed and biodegraded, the time of transport will be the time needed by glyphosate to be biodegraded (time T_{ad}). If glyphosate is adsorbed onto suspended solids and then biodegraded, the time of transport of glyphosate will be the time needed by glyphosate to be biodegraded (T_{sb}) ; if it is desorbed and then biodegraded, it will be transported when it is adsorbed and until it is totally biodegraded (T_{sd}). The system would be similar for diquat and paraquat but more complex because of the importance of photolysis.

In such a compartmentalized approach the river is considered in terms of short sections

of a defined length. Each block of the river consists of several parts that can be defined as suspended solids, benthos, plants, and animals. The transport can be modelled between each compartment and the aqueous phase. In each compartment, several fate processes can be modelled. The main fate processes that govern the transport can be then modelled to and fro each block of the river. Such an approach offers the advantage of the model being able to be validated with mesocosms which would be the physical counterparts of the section of the river. As the river is sectioned a mesocosm can then be setup to reproduce the conditions in the particular section.

4. CONCLUSION

The present paper describes the major fate processes affecting herbicides in riverine systems. Mathematical modelling strategies are reviewed and discussed and a compartmental modelling approach is suggested as a possible approach. Glyphosate, diquat, and paraquat have been considered in this paper because of their wide use in Europe and because of their mode of degradation. Three major processes that affect the fate of these herbicides in rivers are: biodegradation, sorption, and photolysis. Glyphosate has been shown to be biodegraded in soils and to be adsorbed to clay with a rate depending on the unoccupied phosphate sorption capacity, but it is poorly adsorbed to suspended clay in rivers. In the aquatic environment, glyphosate might be degraded by microorganisms that are on vegetation surface, on suspended sediments, or in the sediment after adsorption of glyphosate. Both diquat and paraquat are very rapidly photodegraded in freshwater by UV light. They are also biodegraded in water by microorganisms that use these herbicides as a sole source of carbon or nitrogen. Diquat and paraquat are very strongly adsorbed to sediments and suspended materials, reducing their biodegradation rate and their phytotoxicity because of their unavailability when they are adsorbed. Although many studies have been reported on the adsorption of these three herbicides to benthic sediment, their biodegradation in soil, and photodecomposition of diquat and paraquat in water relatively less work has been performed on their biodegradation behaviour in water.

In many cases, mathematical models are based on the rate of degradation and sorption of pesticides in water and relevant data, in the case of glyphosate, diquat and paraquat, is not always available. Further work is thus proposed in this area. It would be particularly interesting to compare the results obtained from tests on combustion products of these herbicides with identical tests performed on pure products. The importance of such studies goes beyond scientific interest as regulatory pressures continually grow to not only prevent storehouse fire accidents but also to understand the full ecological impact should such incidents occur.

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REFERENCES

- Balthazor, T.M., and L.E. Hallas, "Glyphosate-degrading microorganisms from industrial activated sludge". *Appl. Environ. Microbiol.*, 1986, vol 51, no.2, 432-434.
- Bowmer, K.H., P.M.D. Boulton, D.L. Short, and M.L. Higgins, "Glyphosate sediment interactions and phytotoxicity in turbid water", *Pestic. Sci.*, 1986, vol 17, 79-88.
- Capel, P.D. et al., "Accidental input of pesticides into the Rhine river. Environmental impact and behavior of pollutants discharge during a chemical storehouse fire", *Environ. Sci. Technol.*, 1988, vol 22, no.9, 992-997.
- Chen, Y.H., "Water and sediment routing in rivers", in *Modelling of rivers*, Shen eds, John Wiley & son, 1979, 10.1-10.97.
- Conway, R.A., "Environmental Risk Analysis for Chemicals", 1982, Van Nostrand Reinhold, 549 p.
- Crossland, N.O., D. Bennet, C.J.M. Wolff, and R.P.J. Swannell, "Evaluation of models used to assess the fate of chemicals in aquatic systems", *Pestic. Sci.*, 1986, vol 17, 297-304.
- Corwin, D.L., and W.J. Farmer, "An assessment of the significant physicochemical interactions involved in pesticide diffusion within a pesticide-sediment-water system", *Chemosphere*, 1984, vol 13, no.12, 1295-1317.
- Eisler, R., "Paraquat hazards to fish, wildlife, and invertebrates : a synoptic review", Biological Report 85 (1.22), *Contaminant Hazard Reviews-22*, 1990, Patuxent Wildlife Research Center, Laurel, MD, 35 p.
- Ghassemi, M. et al., "Environmental effects of new herbicides for vegetation control in forestry", *Environ. Int.*, 1982, vol 7, 389-401.
- Grossbard, E., and D. Atkinson, "The herbicide glyphosate", Butterworths, London, 1985, 490 p.
- Gunther, F.A., and J.D. Gunther, "The triazine herbicides", *Residue Rev.*, 1970, vol 32, 413 pp.
- Hallas, L.E. et al., "Characterization of microbial traits associated with glyphosate biodegradation in industrial activated sludge". *J. Ind. Microbiology.*, 1988, vol 3, 377-385.
- Hallas, L.E. et al., "Glyphosate degradation by immobilized bacteria : field studies with industrial wastewater effluent", *Applied and Environmental Microbiology*, 1992, vol 58, no 4, 1215-1219.
- Hance, R.J., "Adsorption of glyphosate by soils", *Pestic. Sci.*, 1976, vol 7, 363-366.
- Hartman, W.A., and D.B. Martin, "Effect of suspended bentonite clay on the acute toxicity of Roundup (glyphosate) to *Daphnia pulex* and *Lemna minor*", *Bull. Environ. Contam. Toxicol.*, 1984, vol 33, 355-361.
- Hill, I.R., and S.J.L. Wright, Eds., *Pesticide microbiology*, 1978, Academic Press, 844 p.
- HMSO, "Assessment of Biodegradability 1981", Methods for the examination of waters and associated materials, published by Her Majesty's Stationery Office (HMOS), 44 High Holbon, London XC1V6MB, ISBN 011 751 6619.
- Hutson, D.H., and T.R. Roberts, "Progress in pesticides biochemistry and toxicology", vol 6, "Herbicides", 1987, John Wiley & son, 286 p.
- Hutson, D.H., and T.R. Roberts, "Progress in pesticides biochemistry and toxicology", vol.7, "Environmental fate of pesticides", 1990, John Wiley & son, 286 p.
- Kearney, P.C., and D.D. Kaufman, "Degradation of herbicides", 1969, Marcel Dekker, New-York, 385 p.

Kenaga, E.E., and Goring, C.A.I. (1980). "Relationship between water solubility, soil sorption, octanol-water partitioning, and concentration of chemicals in biota", in *Aquatic Toxicology* (eds J.G. Eaton, P.R. Parrish and A.C. Hendricks), *ASTM STP 707*, 78-115, American Society for Testing and Materials, Philadelphia.

Mackay, D., "Solubility, partition coefficients, volatility, and evaporation rates", in Hutzinger O. (ed) *A Handbook of Environmental Chemistry*, vol 1, part A, Springer-Verlag, New-York, 1980, 31-45.

Mackay, D.; Paterson, S.; and Joy, M. Application of fugacity models to the estimation of chemical distribution and persistence in the environment. In: *Fate of Chemicals in the Environment*, R. L. Swann and A. Eschenroeder (Eds), ACS. Symp. Ser. 225 (Chapter 9), 1983:175-96.

Mc Connel, J.S., and L.R. Hossner, "pH-dependent adsorption isotherms of glyphosate", *J. Agric. Food Chem.*, 1985, vol 33, 1075-1078.

Moore, J.K., H.D. Braymer, and A.D. Larson, "Isolation of a *Pseudomonas sp.* which utilizes the phosphonate herbicide glyphosate", *Appl. Environ. Microbiol.*, 1983, vol 46, no.2, 316-320.

Muller, M.M., C. Rosenberg, H. Siltanen, and T. Wartiovaara, "Fate of glyphosate and its influence on nitrogen cycling in two Finnish agricultural soil", *Bull. Environ. Contam. Toxicol.*, 1981, vol 27, 724-730.

Neely, W.B., G.E. Blau, and T.Jr. Alfrey, "Mathematical models predict concentration-time profiles resulting from chemical spill in a river", *Environ. Sci. Technol.*, 1976, vol 10, 72-76.

Reinert, K.H., and J.H. Rodgers, "Fate and persistence of aquatic herbicides", *Rev. Environ. Contam. Toxicol.*, 1987, vol 98, 61-98.

Rueppel, M.L., et al., "Metabolism and degradation of glyphosate in soil and water", *J. Agric. Food Chem.*, 1977, vol 25, no 3, 517-522.

Samiullah, Y. *Prediction of the Environmental Fate of Chemicals*. Publisher: Elsevier Applied Science. 1990.

Schnoor, I.L., C. Sato, D. Mc Kechnie, and D. Sahoo, "Processes, coefficients, and models for simulating toxic organics and heavy metals in surface waters", U.S. EPA, EPA-0600/4-87, 1987, Athens, Georgia.

Schnoor, I.L., "Fate of pesticides and chemicals in the environment", 1992, John Wiley eds, 440 p.

Shinabarger, D.L. et al., "Phosphate utilization by the glyphosate degrading *Pseudomonas sp.* strain PG2982", *Appl. Environ. Microbiol.*, 1984, vol 48, no.5, 1049-1050.

Soulas, G., "Mathematical model for microbial degradation of pesticides in the soil", *Soil Biol. Biochem.*, 1982, vol 14, 107-115.

Sprankle, P., W. Meggit, and D. Penner, "Adsorption, mobility and microbial degradation of glyphosate in soil", *Weed Sci.*, 1975, vol 23, no.3, 229-234.

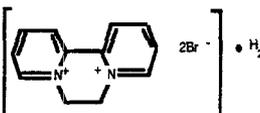
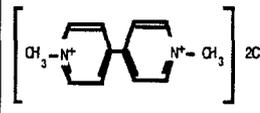
Thomas, W.A., "Computer modelling of rivers : HEC 1-6", in *Modelling of rivers*, Shen eds, John Wiley & son, 1979, 8.1-8.38.

Worthing, Ch.E., "The pesticide manual", 8th ed, 1987, The British Crop Protection Council.

Yoshida, K. et al., "Non-steady state equilibrium model for the preliminary prediction of the fate of chemicals in the environment", *Ecotox. Environ. Safety*, 1983, vol 7, 179-190.

Zepp, R.G., and D.M. Cline, "Rates of direct photolysis in aquatic environment", *Environ. Sci. Technol. J.*, 1977, vol 11, no.4, 359-366.

Table 1 : Properties of Glyphosate, Diquat, and Paraquat
(Worthing, 1987 ; Reinert and Rodgers, 1987 ;
Grossbard *et al.*, 1985 ; Kenaga & Goring, 1980 ; Eisler, 1990)

	GLYPHOSATE	DIQUAT	PARAQUAT
Compound	Organophosphorus	Bipyridylum	Bipyridylum
Structure	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\underset{\text{H}}{\text{N}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{P}}(\text{OH})_2$		
m.p. ¹	200°C	340°C	175-180°C
W _s ²	12 g/l	700 g/l	561 g/l
K _d ³			
montmorillonite	nd	708-2863	nd
kaolinite	66-519	21-57	nd
goethite	102-1826 (depends on pH)	nd	nd
BCF ⁴	low	<1 - 62	nd
Dominant mode of degradation in water	biodegradation (half-life in soil = 60 days)	photolysis (half-life = 48 hr - 11 days) biodegradation (half-life = <15 - 32 days)	photolysis (in freshwater, 50% is degraded in 36 hr, 100% in 4 weeks)
	stable to photolysis and hydrolysis does not bioconcentrate in the biota adsorbed to clay	unstable at 9<pH<12 adsorbed to clay stable to volatilization, hydrolysis and oxidation	oxidized under alkaline conditions adsorbed to clay biodegraded non-explosive, non-flammable, non-volatile
TOXICITY			
Rainbow trout (96 hr)	86 mg/l	21 mg/l	15-32 mg/l
Daphnia (48 hr)	780 mg/l	nd	2.7-4 mg/l
Fathead nimmows (96 hr)	97 mg/l	nd	nd

- (1) m.p : melting point
(2) W_s : water solubility
(3) K_p : sorption partition coefficient
(4) BCF : bioconcentration factor
nd : no data

Figure 1 : Location of pesticides plants in UK

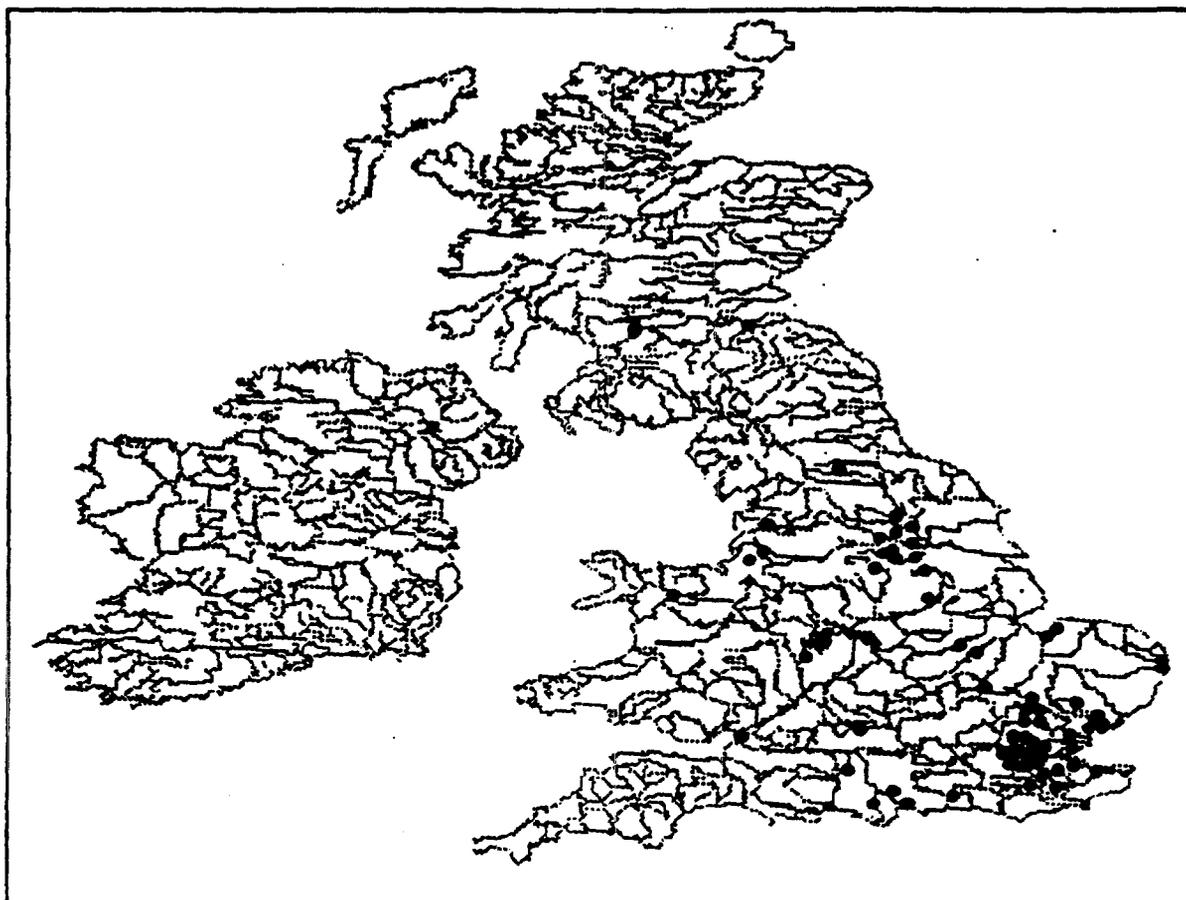


Figure 2 : Interactions between the different compartments of the natural environment : river, estuary, sea, atmosphere, groundwater, and land.

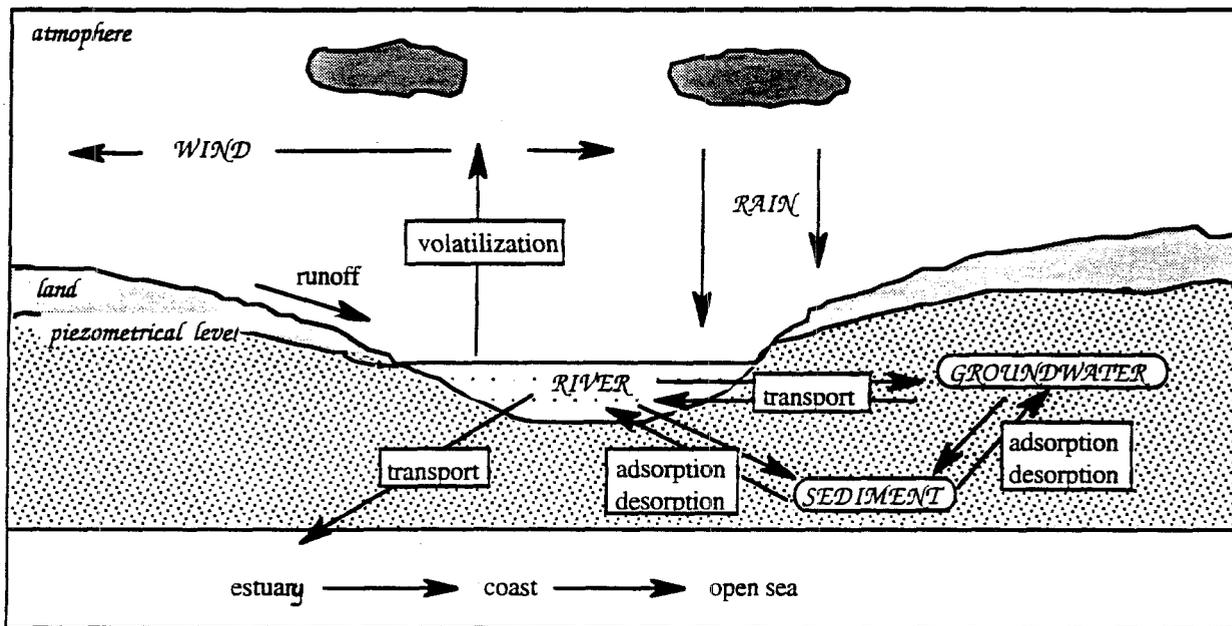


Figure 3 : Fate processes of chemical contaminants in water (After Conway, 1982)

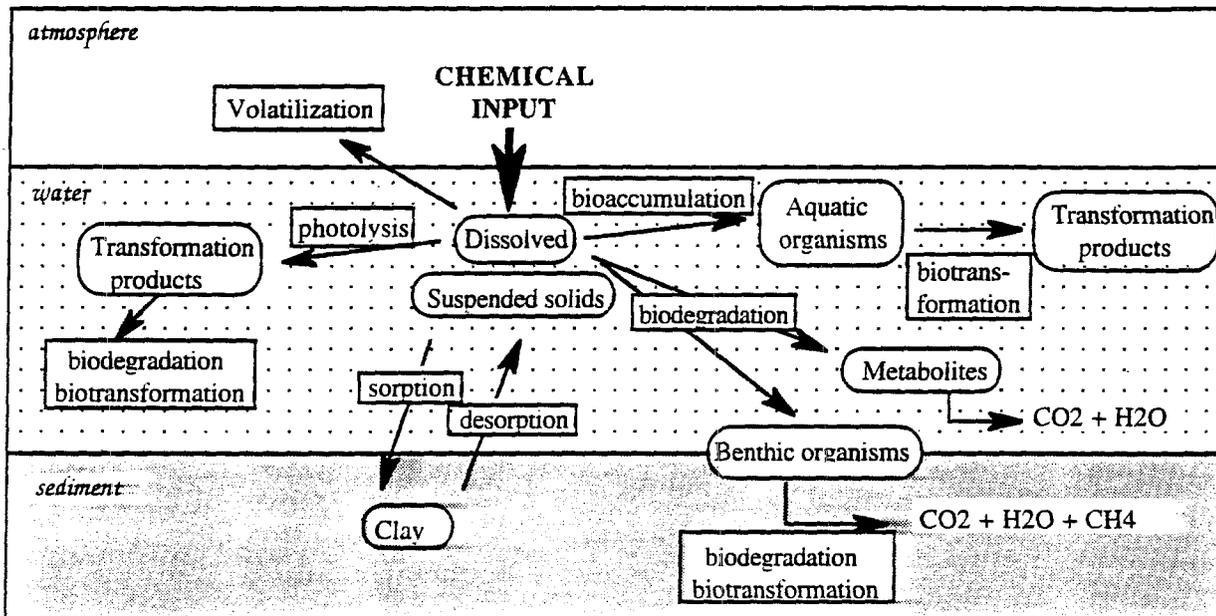


Figure 4 : Multiple pathways for the case of glyphosate.

