

# **Agrochemical pollution risks associated with irrigation in Developing Countries: A Guide**

G R Pearce

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**October 1998**



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# ***Executive Summary***

## **Agrochemical pollution risks associated with irrigation in Developing Countries**

### **A Guide**

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The guide is intended primarily for technical staff who are responsible for the implementation of new irrigated agriculture projects or for the modernisation/rehabilitation of existing ones, and who require relevant technical information to help them assess risk of agrochemical pollution associated with their projects. This assessment would most likely form part of a more comprehensive Environmental Impact Assessment. However, given the concerns particularly linked to agrochemicals, the guide aims to help explain the wide range of complex factors that need to be considered. This guidance is based on consultation of the wide, diverse range of literature that is available, but which may not be easily accessible to practitioners in Developing Countries. The guide brings together the advice and conclusions from the large number of references cited.

Secondly, this guide will also be of relevance officials in Government or donor agencies who wish to understand whether the projects they are interested in supporting may give rise to agrochemical pollution problems. It thus provides non-specialists with an insight into this complex subject and highlights priority issues.

The guide explains the main characteristics concerning agrochemicals, and outlines the typical problems that arise. It is structured to cover the two types of agrochemical:- nutrients (i.e. fertilisers) and biocides (generic term for pesticides and other chemicals for killing unwanted biological organisms). It describes the processes by which agrochemical pollution is generated, and the effects it has on health and the environment. Guidelines are given on permissible concentrations of agrochemicals and how to monitor them.

Details are also given of recent techniques to better manage agrochemical pollution (including details of recognised modelling approach. An appendix gives the use and characteristics of the main biocides in current use around the world. Attention is drawn to particularly hazardous agrochemicals.

The following recommendations are made concerning agrochemical use in Developing Countries:-

- (i) Local arrangements for managing agrochemical usage needs to include a balance of options organised for particular situations. Governments should put in place the necessary legislation and enforce restrictions on the importation of dangerous chemicals.

## ***Executive Summary continued***

- (ii) Monitoring of agrochemical pollution is difficult to implement. There is a need to invest in suitable, cost-effective techniques that will enable authorities to identify the nature of any agrochemical problem before it becomes acute. Environment Agencies need to target likely “hotspots” to ensure limited budgets for monitoring are put to best use.
- (iii) Although pollution problems due to the overuse of agrochemicals are less likely to occur in the short term in many Developing Countries, it is important to raise awareness to avoid problems in the future. They are also often misused and leak into water sources. Better education and extension programmes are thus needed to improve the awareness of farmers.
- (iv) Training programmes need to be established that better equip local officials to deal with potential problems in the provision of agrochemicals. These should be part of initiatives to establish an effective enabling framework that also comprises: Best Management Practices, Legalisation, Monitoring and Compliance.
- (v) This guide can serve as a basis for local awareness and capacity building programmes to educate users and train regulators and other officials in the correct use of agrochemicals.
- (vi) This report is intended to act as a resource that enables concerned professionals in Developing Countries to identify and understand the crucial issues and to identify where to access the large amount of information that is distributed across a very wide number of books, papers, reports and other publications. In order to facilitate this accessibility, it is recommended that copies of this report be sent to the libraries operated by relevant agencies such as the British Council and other bodies.

## ***Glossary***

Acaricide	Kills mites and ticks
Absorption	Process by which a particular substance is soaked up into the volume of a solid
Adsorption	The accumulation of a particular substance onto the surface of a solid as a thin film.
Ammonia (Ammonification)	Colourless, pungent gas, soluble in water and formed by bacterial decomposition of urea (also protein and purines) as part of the denitrification process.
Azolla	Aquatic floating fern increasingly used in flooded rice fields as a green manure to provide organic nitrogen that can later be converted to nitrates for the crop fertilization. Blue-green algae in the azolla's fronds fix nitrogen and then secrete nitrogenous compounds into its tissue.
Biocide	A generic term for the range of chemicals, and other treatments, that are capable of killing living organisms these include pesticides, herbicides, fungicides and insecticides.
BMP	Best Management Practice.
Chemigation	Irrigation with chemical doses of nutrients, biocides and other additives dissolved in the water.
Denitrification	The loss of nitrogen in soils by either biological or chemical mechanisms. This is a gaseous loss and is not related to loss by physical processes such as leaching.
Desorption	Release of chemical compounds from being attached to soil particles (reverse to adsorption).
Eutrophication	The enrichment of natural waters, especially by compounds of nitrogen and phosphorus, resulting in over-rich levels of organic and mineral nutrients. This can lead to profound overpopulation of algae, so that when they die and decay they impose a heavy oxygen demand on the water.
Fertigation	Irrigation with doses of nutrients and other additives included in the water supply.
Fixation	Process of combining a gas with a solid.
Immobilisation	The conversion of mineral nitrogen to organic nitrogen

## ***Glossary continued***

IPM	Integrated Pest Management - use of pest control tactics only when necessary (i.e. not pre-emptive) in a minimalist and compatible manner that maintains side effects at an acceptable economic level
Mobility	The freedom of biocides to move, reflecting whether they are attached to fixed soil particles, whether they are dissolved in water or whether they are retained in their original form (e.g. powder)
Nematocide	Kills nematodes (worms) both free-living and parasitic
Nitrification	The biochemical oxidation of ammonium to nitrite and thence to nitrate by the action of bacteria (soil nitro-bacteria), thereby making nitrogen available in a form usable by plants.
NPK	Nitrogen, Phosphorus and Potassium (K) as a fertilizer usually expressed as a relative ratio of requirement
Persistence	Resistance of chemicals to degradation (given as a half-life).
PMCL	Proposed Maximum Contaminant Level.
Solute	Substance dissolved in water, or other liquid
Sorption	General term for the processes of absorption and adsorption
Translocation	Transport of agrochemical compounds (nutrients or biocides) from one position (e.g. in crop) to another (e.g. to groundwater), or transport within a plant.
Urea	Slowly soluble and relatively stable organic salt of nitrogen that originates from animal urine. It is very soluble in water, highly nitrogenous, and widely used for fertilizer.
Urease	Enzyme produced in many plants that converts urea to ammonium carbonate.
Vadose zone	Soil profile above the water table in which soil water can flow but in a non-saturated phase.
Volatilization	Change of solid (or liquid) [phase of a substance into vapour – refers in particular to the loss of ammonia gas from the soil



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# 1. INTRODUCTION

## 1.1 Aim of guide

The aim of the guide is to provide relevant information on the agrochemical pollution problems that may develop with particular respect to irrigated agriculture in Developing Countries. It describes some of the problems that have been observed in existing schemes, and discusses how the risk of irrigation schemes transferring agrochemical pollution to surface and groundwaters can be evaluated.

The guide describes the types of problems encountered from agrochemical use (Section 2) and then discusses the characteristics of the two main classes - nutrients (Section 3) and biocides (Section 4). In Section 5 it describes the principal mechanism by which agrochemical pollution is transmitted, and in Section 6 what the effect of such pollution is on public health and on the local environment. Existing guidelines developed by relevant authorities on permissible concentrations are given in Section 7. Section 8 discusses how irrigation planners and development authorities should assess the possible risks of agrochemical pollution for their projects. The guide outlines (Section 9) some management options for the use of agrochemicals and for controlling the pollution that may result. Section 10 gives recommendations on monitoring agrochemical pollution in water, on the need for agrochemical use to be more environmentally sustainable, and on training needs.

## 1.2 Target readership

The guide is intended for use by practitioners involved in various water related activities, such as irrigation planners, water resource engineers, development planners and environmental officers. It is intended to help them in assessing the probable environmental impacts of planned irrigation and drainage schemes and in evaluating the actual impacts of operational schemes. It is intended for those who develop irrigation systems (designers) and those responsible for managing the systems, particularly non-specialists who do not have access to experts but need to understand the related problems they may have to deal with. The guide is also of relevance to officials in Government and donor agencies in helping them to assess agrochemical pollution problems in Developing Countries, and in prioritising actions to solve related environmental problems.

## 1.3 Background

Although this guide uses a number of references relevant to Developing Countries, the majority of technical work completed has been carried out in Developed Countries which have very different, generally temperate, conditions. Developing Countries tend to lie in tropical and semi-tropical zones where the climatic and pedological (soil) situation is very different. In arid and semi-arid regions, where irrigation is of prime importance to agriculture production, the climate is characterised by high evapotranspiration rates and insufficient (but sometimes intensive) rainfall. However the beneficial effects of adding irrigation water may be lost by increases in weed and pest populations, and by loss of soil fertility. Thus the use of agrochemicals to preserve benefits can be an important part of strategies for irrigated agriculture. The onset of salinity and soil erosion are also major considerations but they are outside the scope of this report and are dealt with in the two other reports in this Environmental Guidelines series (Lawrence, 1997, Abbott and Hasnip, 1997).

The chosen method of irrigation also has implications. Surface irrigation has unavoidable water wastage which can lead to problems of waterlogging/salinity, as well as encouraging agrochemicals applied on the soil surface to be carried through to the drainage system. Sprinkler irrigation, when well managed, and drip irrigation use only the water that the crops need and therefore cause less drainage problems.

There are a number of socio-economic factors particular to Developing Countries. Principal amongst these are:- a lack of awareness of potential risks, the absence of the monitoring and assessment of environmental problems (such as agrochemical pollution), the rapid growth of populations and the difficulty in controlling environmental degradation. Pollution assessment is a complicated process. Ideally it requires an

understanding of the components and linkages of a chain that stretches from the underlying causes and consequent effects, through to perceptions and costs (Conway, 1991). However, to follow through this process to complete an assessment is difficult and expensive. In Developing Countries the situation is often exacerbated by growing water shortages and the speed with which new pollutants become available. Also there is a continuing problem with the unofficial use of toxic, persistent agrochemicals that have been banned elsewhere in the world.

The world population, currently at 5.7 billion (1995 figures), is predicted to reach over 9.3 billion by the year 2050 (United Nations 1997). The increase will be mostly in Developing Countries (Fischer, 1996) and in Asia in particular. In order to match the growing population, the food production rates, already dramatically increased during the green revolution of the 1970's, will have to increase still more. The food production increases needed may be achieved, at least partially, by:

- (i) the introduction of HYVs (High Yield Varieties of crops)
- (ii) increasing the amount of land under cultivation (either by developing new areas, or by increasing the cropping efficiency on existing cultivated land)
- (iii) higher productivity through the addition of agrochemicals, in the form of nutrients and biocides (the experiences of countries with highly developed agricultural systems over the last 100 years has been that yields can be increased by over 60% if fertilizers and manures are used)
- (iv) higher productivity through the introduction of irrigation.

Increased demand for water has already lead to widespread pressure on the irrigation sector in some countries to use water of marginal quality. The issues surrounding the use of marginal quality water are discussed in an associated guideline report (Abbott and Hasnip, 1997).

The consequence of this situation is an immense challenge to the governments of Developing Countries, to their Development Authorities and to the International Agencies with responsibilities to support such development. Not only will planners have to cope with providing the facilities for the growing populations but also will have to provide the facilities for increased food production and the means of disposing of the wastes produced. At the heart of this challenge is the provision of suitable water supplies - not only for municipal supply and industrial use but also for irrigation. This means that water resources, already under considerable pressure in some countries, will need to be efficiently used and to be protected from unacceptable pollution levels. This raises a fundamental dichotomy. Irrigated agriculture as the major user of water supplies inevitably adds pollutants to the water it uses causing partial degradation of downstream supplies. As irrigated agriculture continues to develop, there will be more use of agrochemicals. This may result in greater pollution levels and hindrance of development downstream. This will be further complicated by the industrial and municipal sources that increasingly coexist with the agricultural sector.

This situation has been widely discussed by development experts in terms of the "Limits to Growth" and the predictions of Malthus, and appears to be quite gloomy. However at a practical level, the problem is not insurmountable. Developing Countries have the opportunity to gain from the experience and mistakes of others, and to ensure that their new investments in agriculture are set up on a sustainable basis and that the by-products and wastes produced are controlled to levels that are acceptable to downstream users.

This guide suggests a wide range of considerations that can immediately be taken up in planning water-related development.

## 2. AGROCHEMICAL POLLUTION PROBLEMS FOUND IN IRRIGATION SCHEMES

Although, the use of agrochemicals is essential to increase crop productivity, there is a need to plan how any undesirable impacts should be mitigated.

### *Nonpoint pollution from fertilizers*

World consumption of fertilizers has been increasing at an average rate of 6% in the last decade (FAO, 1992), reaching a total consumption of over 140 million tonnes. Whilst consumption of nitrogen fertilizers is almost evenly divided between developing and developed countries, developing countries are currently using about 38% of the total world consumption of phosphates. Figure 1 (July, 1993) shows the increasing use of fertilizers per unit area in different parts of the World. All show an increasing trend - developed countries as well as developing countries. However, extra nutrient application does not necessarily mean that more nutrients will pass through the system and reach the downstream users, the farmers operations have a more direct effect on how much passes through (Ongley, 1996). The increased usage of fertilizers can be correlated with enhanced land productivity and hence higher population densities of people and livestock. Consequently, these areas and the groundwater below are being exposed to increased non-point discharges of agricultural wastes.

### *Point source pollution*

Also increases in the demand for agricultural chemicals inevitably promotes the development of new factories and depots where such chemicals can be manufactured and stored. This increases the risk of point-source contamination, and of contamination of surface waterways which interact with near surface aquifers close to rivers and drainage channels into which effluents may be discharged.

### *Spatial distribution*

The spatial distribution of agrochemical pollution in the environment is complex, and depends:-

- (i) on the pattern of human settlement and development, and especially
- (ii) on which crops are adopted locally and what specific requirements they have for supplementary nutrient supply and pest management.

### *Temporal distribution*

The application and usage of agrochemicals also affect the risk of environmental contamination in different locations at different times. The seasonality of each crop dictates the most effective times of applications of nutrients, but also governs the times of emergence of their specific pests and diseases. So the application timing for biocides also depends on crop timing.

### *Soil chemistry effects*

The mobility and decay rates of different agrochemicals result in patterns of contamination in both space and time which are difficult to predict confidently. Also there is chemically interactive relationship between nutrients/biocides and soil particles, which is strongly affected by the presence of air and water in the soil. Adsorption, desorption, decay rates and biological detoxification and transfer all play a part in determining where and how quickly any chemical contaminant will move. Many activities can profoundly affect these interactions. For example, the short- and long-term application regimes of irrigation water can alter groundwater levels, soil oxygen availability, and the biological characteristics of the soil microfauna. These changes can greatly affect nutrient leaching, biocide decay, detoxification, bio-accumulation and transfer to the groundwater aquifers. Soil pH management, for instance, by the application or withdrawal of liming, can significantly affect the mobilisation of agrochemicals.

The technical information available about agrochemical usage currently taking place in the irrigation schemes of developing countries, and on current levels of agrochemical pollution affecting them, is quite limited. Such information, although readily found in developed countries such as USA and Europe, is not widely collected in developing countries.

Furthermore, the information that does exist, when considered along with assessment of the likelihood of pollution emanating from irrigation schemes, suggests that such pollution is generally limited and occurs at a far lower scale than the corresponding agricultural sectors in developed countries.

Most of the risk of biocide pollution comes from the movement of soil particles onto which they have attached themselves (adsorption). Most of the large irrigation schemes that dominate many developing countries are located on low flat river plains where soil erosion is not significant. The principal risk in these situations comes from the application of long-lived (persistent) pesticides, which can leach through, to surface waters or groundwaters. An example of this is the use of DDT pesticides applied not for agricultural reasons but to control mosquitoes as part of Public Health malaria prevention campaigns.

The principal risk for irrigated agriculture in up-country regions is exactly the same as for rain-fed agriculture, in that where natural vegetation has been removed to permit new agricultural development (irrigated or rainfed crops), the erosivity of tropical rainstorms is sufficient to induce substantial removal and transport of top soil. This when moved in suspension - in the run-off or in the surface drainage system - results in pesticides adsorbed on to soil particles being transported to downstream areas.

The objectives of the water resources planner in considering the effects downstream of agrochemical pollution from new, existing or modernised irrigation and drainage schemes are to ensure safe, sustainable provision of:-

- supply for irrigated agriculture
- supply for human/municipal consumption
- supply for industrial use
- safe disposal of concentrated polluted water (either to sea or suitable sink)
- minimum disturbance to ecosystem

At the same time the planner must also consider the quality of water coming down from the upstream areas of the catchment, and how that may affect the way that he uses that water on the irrigation scheme. In this respect upstream agrochemical pollution is unlikely to affect irrigated agricultural operations, but it may have considerable bearing on the supply to new communities on that scheme and on the quality of water stored in any on-line reservoirs.

#### *Penetration of excess agrochemicals to drainage water recycled for irrigation in Egypt*

There is increasing concern about the general levels of pollution in Egyptian water courses, especially as the water is often used for domestic purposes in rural areas (EEAA, 1992). Groundwater contamination has occurred due to extensive irrigation and also widespread application of nitrogen, phosphate, and potash fertilizers. The use of such fertilizers increased fourfold during 1960-1988.

The increase of average concentrations of nitrogen compounds in irrigation return flows was found to correlate with increased application of nitrogen fertilizers (NRI, 1992). High concentrations of ammonia and phosphates have been found in irrigation drainage systems (NRI, 1992). Problems observed include:- (i) some pesticide programmes were found to be incompletely designed, (ii) untrained personnel were allowed to apply pesticides, and (iii) lack of effective monitoring. Egypt has a very high application rate of pesticides compared to neighbouring countries, and its rates are comparable with USA/Europe. Irrigation and drainage channels are also at risk from surface run-off from agricultural land as a result of flood irrigation practices which are common practice in Egypt.

The water quality of the River Nile, which is used for irrigation, industrial and municipal purposes, is declining, due to the presence of trace elements, waterborne pathogens and agricultural waste such as fertilizers and biocides. Drainage water reuse is a necessary and common practice in Egypt and has resulted in some pollutants (industrial and municipal as well as agrochemical) being kept within the environment increasing health risks to local users.



#### *Use of persistent pesticides in Argentina*

The agricultural sector in Mendoza Province utilises a wide range of persistent pesticides that possess a high capacity to deteriorate the environment (Chambouleyron, 1992). Contamination of surface waters and increased nitrogen content in the groundwater have been the main consequences. Although local farmers have adopted the no-slope and no run-off mode of irrigation to partly eliminate runoff into the irrigation system, excess water is still reaching the drainage system. Owing to the scarcity of water in the province, drainage water is reused, thus leading to further risks of agrochemical pollution (Chambouleyron, 1992).

#### *Loss of agrochemicals from areas susceptible to soil erosion in Brazil*

In the state of Parana high soil erosion rates have caused losses of natural nutrients such as nitrogen, phosphorus and potassium from the soil. This loss of fertility has led to increased use of fertilizers. At the same time the use of biocides has also greatly increased. The use of agrochemicals such as NPK chemical fertilizers, insecticides, fungicides and herbicides grew respectively between 1970 and 1980 by 444%, 489%, 197% and 1346% (Andreoli, 1992). Studies have shown that the levels of phosphorous, nitrates and suspended solids in the main rivers of Parana have been found to almost double during the months of April/May and September/November, which coincide with periods in which soils are prepared for seed-planting (Andreoli, 1992). There is a lack of analytical facilities for agrochemical residues and there is a need for improved monitoring and modelling.

#### *Pesticide adsorption to soil particles in Colombia*

The intensive cultivation of rice, bananas, sugarcane, cotton and sorghum in Colombia utilises large quantities of agrochemicals which affect surface and groundwaters. Environmental monitoring of 25 large-scale irrigation projects and 200 small-scale irrigation projects has been carried out. In one case-study in the Irrigation District of Saldana (15 000 ha), high concentrations of DDT were identified in soil samples and in the sediment of the canals, and of Methyl-Parathion in irrigation canals (Gomez-Sanchez, 1992).

#### *Direct application of herbicides to channels to control aquatic weeds in Egypt*

Another concern in Egypt has been the treatment of aquatic weeds in irrigation canals with various herbicides. Use of herbicides in water bodies requires close supervision and careful management. Spray drift, accidental spillages and applications at higher than permitted concentrations caused the Egyptian government to ban the use of aquatic herbicides in the early 1990's.

Far more work has been performed on the effects of agrochemicals from irrigation schemes in the developed world. This work has indicated the widespread contamination of surface and groundwater by nitrates and pesticides and the subsequent environmental effects. Goolsby (1991) describes the widespread use of agrochemicals in the upper midwestern US, Gianessi (1988) estimating that in 10 US states over 100,000 tonnes of pesticides were used in 1982. The result in the US of such widespread use of pesticides and other biocides has been the contamination of water sources with reported fish kills, destruction of vegetation due to inappropriate application of herbicides and the rendering of water sources unfit for human consumption. Contamination of water sources by excessive concentrations of nutrients is widespread. In France, Ignazi (1992) describes nitrate levels of 25 to 50mg/l in the water supplied to 95% of the population, the other 5% receiving water with concentrations in excess of 50mg/l. Pratt (1984) and Ludwick (1976) from work in the US have shown irrigation, through leaching, to produce widespread contamination of water sources, the contamination being proportional to the nitrogen fertiliser applied. Power (1989) also showed that deliberate irrigation in order to prevent salinisation can have the undesired effect of flushing agrochemicals into the groundwater or drainage system.

In contrast to the many examples of widespread contamination of water sources within the developed world due to agricultural practices, there are few examples available from developing countries. This is due partly to the scarcity of data, the differences in soils and climatic conditions and to the less intensive use of crop inputs. However, with time more and more farmers and regions are adopting higher intensity farming techniques. Unless they are encouraged to take up more careful management, their increased use of agrochemicals will be accompanied by more widespread contamination.

## 3. NUTRIENTS

### 3.1 Nitrogen fertilizers

The benefit of the greatly increased use of nitrogenous fertilizers, particularly in developing countries, has been a large-scale increase in the productivity of land (See Section 1.3). However these benefits are counterbalanced by adverse effects and the costs of either preventing pollution or correcting affected waters. Concentrations of nitrate in natural waters have been increasing steadily for the past few decades, coinciding with the increased use of nitrogen fertilizers in agriculture. Nitrogen fertilizers contain nitrogen in one of three forms:- ammonium, nitrate or urea. Urea is the most common form worldwide; however, whichever is used, the same type of benefit is achieved in the form of extra nitrate available to crops.

Nitrates are extremely soluble in water, which means that irrigation water or rainwater passing through the soil may easily carry nitrate with it. Ammonium, which is not soluble in water, is converted to nitrate in the soil by microbes, and therefore also contributes to available nitrate over a longer time-scale. Particularly in intensive, cash-crop areas such as USA and Western Europe, the agricultural sector has been encouraged to maximise yields and crop acceptability with the large-scale use of fertilizers. This has led to well-documented wide-scale nitrate contamination of ground waters and surface waters. The nitrogen cycle in irrigation schemes is shown in Figure 2.

It is self-evident that minimising target nitrate levels in the root zone will reduce nitrate loss rates and minimise nitrate pollution of surface and groundwater sources. Whether or not nitrate contributes to pollution depends what happens to rain or irrigation water passing through the soil, which in turn depends largely on the physical behaviour of water in the soil.

#### 3.1.1 Nitrogen transformations

Nitrogen is present in the soil in several distinct forms:- nitrates ( $\text{NO}_3$ ), nitrites ( $\text{NO}_2$ ), nitrogen gas ( $\text{N}_2$ ), ammonia ( $\text{NH}_3$ ) and ammonium ( $\text{NH}_4$ ). The oxidation of organic nitrogen through to nitrate via a number of reactions is called mineralisation (Figure 3). The first step, the conversion of organic nitrogen to ammonium, is called ammonification. Organic matter in the soil, e.g. plant residues, is converted into ammonium by biological activity. In soils that are very acid or permanently waterlogged, ammonium is the final product of mineralisation. However, in most soils ammonium is oxidised by microbes, first to nitrite and then to nitrate in a stage of mineralisation is called nitrification. Nitrification is a specialised process involving a small number of species of bacteria, for example of the genera *Nitrosomonas* and *Nitrobacter*, which are found in almost all soils.

Ammonia is present either dissolved in soil water or is captured by cation adsorption and remains in the soil for a longer period of time. Adsorption by cation exchange is increased if montmorillonitic clays are present (Grillot, 1988). Adsorbed ammonia is released slowly, making it more available to plants. More ammonia is converted to nitrate through nitrification, or lost through volatilisation, than is adsorbed by cation exchange. Nitrification generally occurs very rapidly, before the throughflow of soil-water with dissolved ammonia comes into contact with a sufficiently effective volume of soil for a significant proportion of the ammonia to be removed by cation exchange.

#### *Denitrification*

The mineralisation process is reversible. The soil biomass can also contain bacteria that can destroy nitrates, a process called denitrification. Mainly this process occurs in wet soils. Any nitrate that is denitrified is reduced to ammonia and either dissolved in soil water or evaporates through the soil (sometimes called volatilisation).

#### 3.1.2 Nitrogen distribution in the soil

The climate and the variation of agricultural practices from season to season alter the relative significance of each of the processes in the unsaturated zone of transformation between ammonia and nitrogen. For example, the volatilisation of nitrogen to the air increases as the soil becomes dryer during in the summer

period. The distribution of nitrogen in the soil is also dependent on denitrification processes in the root zone, and on transport processes between the root zone and the water table.

The conversion of ammonia to nitrate through nitrification may decrease nitrate concentrations in the oxidising conditions which exist above the groundwater table in the vadose zone (Gostick, 1975). This will be greater in locations where the drainage is good and where the proportion of active clay to capture ammonia by cation exchange is low.

Nitrate levels also tend to decrease with depth below the water table (Geyer, 1992), because of further biological utilisation of nitrates within the deeper groundwater levels, or lateral transportation of water near the surface of the saturated zone resulting from surface or near-surface drainage channels in the upper levels of the groundwater reservoirs. These lateral flows are quite common in the field as they are promoted by the use of tubewells. Many wells are only deep enough to penetrate the upper levels of the permanent water table, and therefore tend to draw water from the upper levels of water in the saturated zone.

### 3.1.3 Use of nitrogen fertilizer by crops

Crops' nitrogen requirements are supplied as their roots absorb nitrates from the soil. Where soil nitrate levels are insufficient (infertile soil, removal of nitrates by previous crop) then fertilizers can be added to enhance the supply. This can be done using:-

- Fast release fertilizers - chemical nitrates
- Moderately fast fertilizers - Ammonium nitrates which contain nitrates (immediate) and  $\text{NH}_4^+$  which is fairly rapidly oxidised in the soil to nitrate
- Slow release sources - generally organic forms originating as complex, naturally-occurring organic biochemicals, or as urea fertilisers. These all eventually break down to form nitrate in the soil.

Crop requirements for nitrogen are often expressed in terms of their nitrogen content, rather than by reference to their nitrate tolerance. In contrast in matters concerning Public Health, acceptable limits are expressed in terms of nitrate tolerance rather than total chemically-bound nitrogen.

When comparing the nitrate tolerance of crops and the amount of available nitrate supplied by different fertilizers, it is important to compare like with like. Crop requirements are usually expressed in terms of nitrogen content (N-content). The following sub-sections show how this can be compared to the equivalent amount of nitrate (or ammonia) that the fertilizer will generate (HR Wallingford, 1995). Table 1 gives the equivalences for all forms of N-fertilizers. In particular, care needs to be taken to compare data expressed as nitrate or ammonia with that expressed in terms of nitrogen which is linked to these two principal nitrogen-based nutrients.

#### Nitrate

Nitrate salts are extremely soluble in water, and are not found as solid crystalline deposits in normal soils. Examination of atomic weights shows that the nitrate ion,  $\text{NO}_3^-$  contains 21.9% nitrogen by weight; 10mg/l of nitrate therefore contains 2.2mg/l of nitrogen, whilst a nitrogen content expressed as "10mg/l of nitrate nitrogen" contains 45.6mg/l of nitrate.

#### Ammonium

Ammonium nitrate ( $\text{NH}_4^+ \text{NO}_3^-$ ) fertilisers provide two active types of nitrogen for crops to use, since they contain both ammonium and nitrate sources. The nitrogen level is 35% so 28.6 mg/l in soil water is needed to provide 10 mg/l of nitrogen.

#### Ammonia

Ammonia is a toxic gas which dissolves instantly in water to form an alkaline solution of ammonium hydroxide. Never present in damp soils, it may be released when heavily manured soil is limed or when

conditions are alkaline. Ammonia has a slightly higher nitrogen content (82.3%) than the ammonium ion (77.8%), and 10 mg/l of ammonia nitrogen also yields 45.6 mg/l of nitrate on oxidation.

### Urea

Urea is a slowly soluble and relatively stable organic salt of nitrogen, with formula  $\text{CO}(\text{NH}_2)_2$ . It contains 46.7% of nitrogen by weight. In the soil it reacts comparatively slowly with water (hydrolysis) to release two molecules of ammonia. This ammonia immediately dissolves in the soil moisture and nitrifies to nitrate, which crop roots are able to absorb. Urea therefore acts as a slow-release nitrogen source. Its value in the control of nitrate contamination of groundwater is that plants are able to use a higher proportion of the nitrogen as it is released. The nitrate concentrations derived from urea in the soil water in the root zone are relatively low, and less is liable to be leached downward to the water table. Soil water containing urea at a nitrogen-equivalent of 10 mg/l contains 21.4 mg/l of urea; on hydrolysis this releases 12.1 mg/l of ammonia, which oxidises to form the same 45.6 mg/l of nitrate.

## **3.2 Organic fertilizers**

The use of composts and green manures which are naturally rich in nitrogen is well established worldwide especially in subsistence agriculture. As agricultural practices become more intensive, pressure to use alternative sources of commercially produced nitrogen has grown. There is, however, increased potential for the use of biologically-derived nitrogen sources for supplementing or replacing commercial nitrogen sources. The main sources of organic nitrogen are:-

- Human, domestic and urban sewage used as an agricultural supplement (either in the form of dried sludge cake or direct application of sewage effluent),
- Manure from livestock is often directly applied.
- Leguminous plants used as compost or green manure to provide slow release nitrogen sources for subsequent crops,
- *Blue-green algae* (nitrogen-fixing bacteria of the family *Cyanobacteria*), encouraged to develop on the surface of wet or shallow ponded soils, for appropriate nutrition of rice crops (Cross, 1992). For example, the aquatic floating fern *Azolla* which has symbiotic relationships with some crop species is intensively used in rice culture. As rice paddy is inevitably associated with locally elevated water-tables, which are prone to nitrate leaching, this technique appears to offer substantial incentives for further development, since it provides organic nitrogen which is available for a much longer period than nitrate provided by chemical fertilisers.

### *3.2.1 Role of organic material and bacteria in nitrogen mobility*

Bacteria play vital roles in the soil processes of oxidation, nitrification and denitrification, and carry out a similar role to that of sewage purification. Where animal and human wastes are acting as nitrogen supply sources to soils, they may be the most important risk factor in nitrate transfer to groundwater. This is a particular concern in rural areas, e.g. India, where animal dung heaps are located around villages and permit nitrate leaching to groundwater to take place at the very place where well water is drawn for human consumption. Additionally it is worth pointing out that these are the only wells in the area where groundwater samples can be easily taken; and therefore they may give an unreliable representation of the local groundwater situation.

Ammonia from animal and human wastes is converted to nitrate by bacterial action, with a time lag of about a month before peak production rate is reached. Although the process is temperature-dependent, the seasonal differences in ammonia oxidation rates for these wastes are less marked than those which occur in irrigated soils (Chopp, 1982).

Organic products released to the soil, form complex colloids in the soil humus, which help delay the leaching of nitrate from near-surface soil horizons (Norman-Schmidt, 1993). Cellulose and lignin have both been identified as important constituents in reducing nitrate losses, especially from high ammonia animal wastes (Baker, 1992). Since the colloidal carbon sources form the main energy source for denitrification bacteria in the soil, there will be low levels of such bacteria if the carbon source is small. This leads to low conversion

of nitrate into ammonia dissolved in the soil water, and therefore high nitrate losses as the excess nitrate is quickly leached.

On the other hand, in countries where fertiliser application rates are low, such as many developing countries, the amount of nitrogen lost from the soil by denitrification can be too high .

In deoxygenated aquifers, denitrification may provide some capacity for self-purification, since nitrate is converted to nitrogen gas which may be absorbed in the water under pressure.

### 3.3 Phosphate fertilisers

In almost every agricultural system farmers routinely apply substantial amounts of phosphate fertilisers to the soil, as well as nitrogen, ammonium and potassium fertilizers. On the whole agricultural phosphates do not create substantial pollution problems. The phosphate pollution problems seen in surface water bodies (deoxygenation due to algal blooms, Conway,1991) are usually directly attributable to municipal and industrial wastewaters. In particular, the role of domestic sewage and phosphate detergent have been identified as major causes. In contrast there is little evidence of phosphate pollution from agricultural sources (such as fertilizers or farm waste). Normally phosphates are at a level below that required for balance with nitrates (approximately 10-20:1) and are the limiting factor. The phosphorus cycle in irrigation schemes is shown in Figure 4.

Phosphates are strongly absorbed by iron and aluminium hydroxy-oxides in the soil and are retained in the profile for long periods of time. Phosphates in soil solution move in a similar way to nitrates. However the amount of phosphates that actually move in the soil solution is very low compared with the total amount of phosphates held in the soil. In most agricultural soils, the process of phosphate sorption retains applied phosphates within the soil profile and in surface waters acts rather as a phosphate sink than a source.

Phosphates in the soil are much less mobile than nitrates. They generally do not represent a significant risk to groundwater quality. Heavy application of phosphate-rich fertilisers may lead to phosphate saturation of the soil (Hopstaken, 1989), and to a substantial increase in organic phosphorus in the surface layer of the soil. But phosphate leaching is rare and occurs only at high overload levels. Even then it tends to be only close to the surface, generally to depths of around 0.6m (Latterell, 1982). In the USA (Turner, 1979), even after tile-drained silt-loams had been overloaded by inorganic fertiliser, less than 2% of the added phosphate was lost through the drainage system. Similarly, studies in Portugal (Comans, 1987) showed that phosphates were rapidly immobilised in the soil, and were not concentrated in the root zone, even under conditions of intense evapotranspiration by the covering vegetation.

The main mechanism by which phosphate is lost from fertilised soils, is the adsorption of the soluble phosphate onto soil particles, which are then eroded by erosive surface run-off. In some cases this accounts for 75% of the total phosphorus loss from some soils appears to be particulate, with the greatest losses occurring from rotationally-cropped watersheds. In the Netherlands, the main cause of contamination of surface waters by agricultural phosphates was inadvertent placement in agricultural ditches.

### 3.4 Potassium fertilisers

Most agricultural soils show fairly high crop uptake efficiencies for potassium fertilizers. Potassium leaching losses on clay soil are frequently reported as insignificant (<2%), although, up to 70% leaching losses have been reported on a sandy podzol.

Studies in the USA on potassium leaching related loss rates to the use of chemical or organic fertilizers. Soils with high rates of organic matter application (in the form of digested sewage sludge) lost twice as much potassium through leaching as plots on which inorganic fertilisers were applied (during a normal rainfall year). However, in a dry year it was the fertiliser-treated plots that lost more potassium (30% more). To put this in context, the overall losses of potassium from all plots were small compared with the amounts supplied in sludge and fertiliser, and with the total amounts of potassium in the soil. The highest losses occurred during surface run-off after heavy rain, and during the winter snowmelt period (Jones, 1986).

## 4. BIOCIDES

### 4.1 Uses in agriculture

The use of biocides for pest and disease control in crop production continues to play a central role in ensuring adequate food supply for the growing world population. Crop productivity on available agricultural land needs to be intensified. In many developing countries there are only marginal possibilities for extending agricultural land – much of the suitable land has already been fully developed so the yield potential of crop plants has to be secured against detrimental effects, such as pests and diseases.

One emerging trend is the growing resilience of pests to the biocides developed to control them. This trend is worsened by the perverse situation that some target pests are even thriving because the natural predator enemies that control their population, have been more seriously affected by the applied biocides.

A second trend has been the downstream pollution caused by the use of more persistent biocides. This has been a significant problem more in developed countries where wide-scale use has been practised on a preventative basis (i.e. the biocides are applied even if the target pests are not at a significant level) rather than on a reactive basis.

Whilst the second trend has been largely dealt with by the discontinuation and banning of persistent pesticides, and by the slow take-up by subsistence farmers who cannot easily afford expensive chemicals, the first trend is still a problem in developing countries. In some cases it is difficult for the pesticide manufacturers to come up with new formulations that are effective. The solution may well be for the agricultural sector to be more prepared to coexist with the pests and to control their numbers by more eco-friendly techniques (such as less virulent pesticides and IPM) rather than continuing to seek the unattainable objective of totally eradicating them from their fields.

### 4.2 Types of biocide

Main classes:-

- Organophosphates (OP)
- Organochlorides (OC)
- Triazines
- Phenoxy-carbon acids
- Organometals
- Carbamates
- Pyrethroids
- Inorganics

### 4.3 Risks of biocide contamination

Percolation rates of biocides through groundwater systems tend to be relatively slow; consequently, the translocation of even mobile biocides from the surface to deep aquifers takes years, or even decades, rather than weeks. This lag period makes it ineffectual to monitor deep well waters for such contaminants when attempting to keep track of the effects of relatively recent or short-term changes in biocide application patterns. Existing biocide residue concentrations cannot show trends because:-

- levels measured at any given time may represent a situation in which historical usage is causing a gradual increase in the level of contamination, or
- levels measured may be equilibrium levels which reflect the complex inter-relationships between the different rates of application, degradation, translocation and dilution within the aquifer itself, the aerated vadose zone above it, and the biologically active root and surface zones.

#### 4.3.1 Biocide persistence

Biocides that are not lost by volatilisation or in run-off, enter the soil and are either adsorbed to the soil structure, held in the soil-water-air continuum or are leached through the soil profile into the groundwater.

Some biocides degrade readily in the soil; others, particularly the organochlorines, resist degradation for very long periods (decades). Occasionally, the products of the degradation process can also be as toxic, or even more toxic, than the original pesticide. Table 2 gives the persistence for several types of pesticides.

#### 4.3.2 *Biocide persistence in the soil*

The length of time that pesticides remain in the soil is dependent on the soil type and its capacity to adsorb active compounds. The method by which they were applied also has an effect. In general, the soil absorptive capacity is highest in organic rich soils, and is least in sandy soils. For instance in the case of DDT, which is strongly adsorbed in all soils, the ratio of absorption between a sandy loam soil, a clay soil and an organic rich soil was 1:10:80 (Shin, 1970). Soil type makes a considerable difference to the length of time the pesticide is usefully located at the target and how quickly it may move to another location. If the pesticide is applied by mixing it with the soil, the residence time is greatly extended (from 1-2 years extended to 25-40 years for 95% disappearance, Wheatley, 1965).

The pesticides that are not held in the soil matrix or degraded, are able to be leached down through the root zone and possibly into the underlying groundwater. This in the past has widely been assumed to be insignificant, but recent field results in the 1970/80s showed that penetration can occur under certain susceptible conditions. In the USA, the susceptibility was due to shallow sandy soils with high water tables and low organic carbon content. In the UK it was due to fast flow through fissured rock and low organic matter (Conway, 1991). The main determinants of pesticide leaching are the type of soil/rock overlying and comprising the aquifer. Irrigation also increases pesticides leaching because it increases downward flows of water. The compounds likely to leach are the water soluble herbicides (such as TCA, mecoprop MCPP, MCPA, 2,4-D and dienseb) and insecticides (such as dimethoate).

Soil pH also has an effect on the half life of a compound. The half life of aldicarb at pH 6 is 23 years whereas at pH 8 it is only 82 days (Conway, 1991).

#### 4.3.3 *Mobility of persistent biocides*

Some biocide-soil combinations result in such strong binding of the biocide to soil particles that the biocide is moved only if the soil is moved, i.e.. if soil erosion occurs. Only biocides that are relatively persistent and mobile will be capable of leaching to groundwaters because the travel time for water to percolate to deep aquifers can range from months to years. Persistent and mobile biocides are also more of a threat for runoff. Biocide runoff is much less dependent on biocide properties than biocide leaching, and much more dependent on how soon runoff occurs after application.

Biocide mobility in soils is related to their susceptibility to adsorption by soil organic materials and clay minerals. Chlorinated hydrocarbons in soil generally take 3-6 months for a 95% disappearance (Paasonen-Kivekas, 1989). However, whilst many biocides tend to become rapidly immobilised in the upper soil horizon, some, which are strongly adsorbed onto colloidal particles, may be translocated fairly rapidly in aquifer flows if they are in coarse-grained strata. In alkaline soils some biocides, such as atrazine, may be degraded by hydrolysis, whilst other acidic compounds (e.g., carboxylic acid herbicides such as Mecoprop) may form insoluble calcium derivatives. The partition coefficients relating the affinity of biocides to organic matter are often quoted as indications of their relative mobility (Johnson-Logan, 1992), but this may be misleading (Kan, 1990) because sandy soils, particularly on aquifer outcrops, or in areas of high rainfall or intensive irrigation are much more prone to biocide leaching than silt loams (Kladivko, 1991).

Some hydrophobic biocides in soils may be passively transported by mobile bacteria. The partition coefficient between water and the lipids of the bacterial membranes is commonly as high as 250 to 14,000 (for example DDT and HCH) and the presence of large populations of soil bacteria may result in very substantial increases in the transport rates (by factors of 8 to 14) of these chemicals as the bacteria are moved by the percolation of the water through the soil (Lindqvist, 1992).

## 5. MAIN MECHANISMS FOR AGROCHEMICAL POLLUTION

This section discusses the main mechanisms by which nutrients (see Section 5.1) and biocides (see Section 5.2) cause pollution problems. There are many factors that can lead to pollution, either independently or in combination with others, when agricultural chemicals are used in irrigation schemes. In developing countries, many agrochemical pollution problems result at least in part from insufficient knowledge at a practical level about the potential hazards involved. Each problem has its own particular causes. Often pollution is caused by increased inclination to overuse agrochemicals in order to increase fertility to levels that are not actually needed, or prevent pest attacks that are unlikely to take place (Conway, 1991).

### 5.1 Nutrient mechanisms

Fertilizers, although not designed to kill life, can play an important role in chemical reactions in the environment that do result in significant pollution. Nitrates and phosphates leached from the land on which they were applied can result in eutrophication of rivers, lakes and coastal waters, and may be converted in humans and other animals to produce toxic nitrites (Conway, 1991). Figure 5 shows the nutrient loss process.

#### Leaching

Irrigation in arid and semi-arid regions has the effect of enhancing nutrient losses because of the need to leach for salinity control. In addition to the unwanted salt, irrigation leaching will also transport nutrients below the root zone. Achieving a balance is difficult since the objective of adding fertilizers is completely opposite to leaching salts down and aims to leave the added nutrients in place for as long as possible in the root zone.

The amount of nitrate which actually leaches to the groundwater resource is dependent on:- (i) the volume of irrigation water; (ii) the actual concentration of soluble nitrate in the root and vadose zones, and (iii) the dynamic rates of uptake by plants and microfauna in the soil (Katzur, 1983). When the root zone overlies an impermeable layer, the probability of nitrate leaching into the groundwater is reduced (Muller, 1982). However, where soils are more permeable, the risk of nitrate leaching to shallow aquifers is increased by the soil's high hydraulic conductivities and low attenuation capacity (Mossbarger, 1989). Once the agrochemicals reach the groundwater they may flow along and concentrate close to the top of the water table if hydraulic gradients favour lateral movement, which may result from local borehole abstractions.

The irrigation water should also be tested for nitrogen content so that the nitrogen fertilizer rates can be adjusted accordingly.

Soil type and crop type influence the extent to which applied irrigation water leaches nutrients. Irrigation, for example, on coarse-textured sandy soils and with shallow-rooted crops, increased the chances of nitrate leaching (Schmitt, 1993).

If fertilizer is applied with the irrigation water (a process called fertigation), the nitrogen application uniformity depends on the irrigation uniformity. It is possible that some of the nitrogen supply may flow back into the irrigation water source. For this reason, fertigation is only suitable for use with systems that can provide a uniform water application over the entire field.

#### Run-off

If the rate of water application is higher than it can infiltrate into the soil, then surface run-off, or flow to surface drains, may introduce a pulse of unabsorbed nitrate into the natural drainage system.

#### Uptake rates

Rates of uptake range from 40-80% for applied nitrogen and 5-20% for applied phosphorus. As more fertilizer is applied, uptake becomes less efficient.



### Movement of soil particles - soil erosion

Soil erosion is the principal process by which adsorbed nutrients such as phosphorus are transported into downstream surface waters. In sandy and/or organic soils, phosphates cannot be transported away by clay, oxide, and carbonate particles and are generally retained in the soil. Phosphorus adsorbed on to the surfaces of soil particles that are transported by erosion can desorb back into solution as soluble phosphorus is diluted and can thus help accelerate any eutrophication problem in downstream water bodies. Phosphates can be the major pollutant of surface water where eroded soils are being deposited in bodies of water (Klaassen, 1986). Eutrophication of surface water can be caused by incoming waters with P concentrations even lower than 1 mg/l. Control of soil erosion is thus often the key preventing phosphorous problems in surface waters.

## **5.2 Biocide mechanisms**

In response to the growing use of pesticides, there has been an upsurge of resistant forms of plant pests and disease vectors (WHO, 1980). Chemicals no longer provide the same level of protection to plants as formerly. In response to the heavy use of pesticides, the pests themselves have evolved resistant strains. These have mechanisms for neutralising and avoiding pesticide attacks. The result of this has been a requirement for more chemicals to be developed to deal with the resistant forms of pests. Many of the more effective pesticides that have had to be introduced pose greater environmental hazards for pollution than previous chemicals.

In an agricultural crop system there are three locations (called compartments) where biocides may be applied - (1) direct to the plants, (2) to the soil surface, and (3) to the soil below the surface. Each compartment can lose pesticides by degradation, evaporation, and other dissipation processes. The biocides, as illustrated in Figures 6 and 7, may reach both ground and surface waters by several pathways, including surface runoff, erosion, leaching, spray drift, improper disposal of containers and accidental spills (O'Neill, 1990).

Irrigation technology can govern the fate and transport of a pesticide in soil through control of the soil moisture regime. Various processes, such as sorption-desorption, volatilization, and degradation are influenced by irrigation. Gravity, sprinkler, and drip irrigation methods differ significantly in the way that water is conveyed to the field. This means that the way that water enters, and moves through, the soil is very different, and has profound effects on whether there is any runoff and whether agrochemicals will be leached, removed or left in place.

Very few pesticides are applied directly to water. It is, however, still possible for some to reach water through spray drift or translocation to sub-surface water. Spray drift and run-off are primarily responsible for pesticide occurrence in surface waters. The physical properties of any given pesticide will govern the extent to which it is absorbed into the soil and is prevented from moving. Pesticides rarely reach the groundwater because they are generally absorbed in the soil matrix. But as mentioned in Section 4.3.3 it is possible for them to penetrate through if a carrier such as colloids or bacteria is leached through, or if they have some solubility.

Pesticide run-off can be caused by rainfall run-off on irrigated areas - such as the effect of monsoon rainfall on low-lying flat irrigated lands. A very significant cause of pesticide run-off is the soil erosion caused by heavy rainfall on sloping lands where natural vegetation has been cleared. It is important to note that this is just as applicable for areas cleared for rainfed agriculture as those cleared and graded for irrigation (e.g. furrow irrigation).

### Surface run-off

Biocides may be lost in surface run-off either carried away on soil particles on to which they have been absorbed, or transported in the dissolved state. Applying soluble biocides to the soil results in the highest

proportion of loss in surface run-off. There is less loss from fallow fields than from cultivated fields, where applied biocides penetrate more deeply into the root zone.

The susceptibility of different biocides to be lost in the runoff from sloping land can be described using the 'Coefficient of entrainment' (Meeks, 1990). This parameter provides a means by which the risk of moving the biocides can be compared, for example:

- *chlorinated hydrocarbons* - tend to have a coefficient of around 1% of the applied amount
- *triazine herbicides* (usually applied in the form of a wettable powder) - tend to have coefficients of around 2% for slopes of 10° or less, and up to 5% on steeper slopes.

For biocides applied directly to the soil, the coefficient tends to fluctuate, but does not exceed 5%. Coefficients of stable biocides such as DDT, HCH, etc., have coefficients of the order of 0.01 to 0.1%, depending on conditions. Organophosphorus compounds tend to have greater water solubility, are more mobile, and have coefficients of 5% to 10%.

#### Lateral leaching into surface drainage systems

This is a very significant process. The factors controlling the rates of transportation of biocides into surface drainage systems are their persistence and sorption coefficients. The mechanism for the lateral leaching of biocides is the same as for vertical leaching to groundwater. However the pathway is much shorter and in the situation of a strong hydraulic gradient driving flow to the drains, substantial components of applied mobile pesticides can emerge in the lateral drains in a short time (order of hours/days) and well within the half-life of less persistent pesticides.

This process can be further simplified in certain cracking clay soils when water application is made (see sub-section 5.2.10). The wetting front passes across the surface of soil columns picking up soluble biocides and passes through the macropore system of the soil without significant interaction with the soil to adsorb the biocides. This results in the quick emergence of a pulse of active pesticide into the field drains and into the receiving surface water system.

Recent studies on the translocation of biocides into drainage systems have shown:-

- (i) Aldicarb (and its degradation product aldoxycarb) were found to have a half-life in soil of 0.2 to 2.1 months (Jones, 1986), and to be leachable to maximum depths of 0.6m to 1.8m. This means that, under normal agricultural conditions, Aldicarb would not be expected to reach the groundwater or the drainage system.
- (ii) Leptophos, an extremely persistent organophosphate insecticide, was found to degrade extremely slowly in Nile water (Riskallah, 1979) and poses a risk in drainage return flows.
- (iii) With relative mobilities of biocides related to their sorption coefficients, recent US results detail how carbofuran, atrazine, cyanazine and alochlor were found in drainage ditches three weeks after application, whilst chlorothalonil and carbofuran appeared in groundwater within four weeks (Krawchuk, 1987).

#### Translocation from the cultivated zone to the water table

Translocation of biocides from the surface of agricultural land to groundwater can rarely be accounted for just by simple diffusion pathways. As for nitrates and ammonia, chemical and biochemical transformation processes affect the mobility, degradation and ultimate fate of biocides in soil. The rate at which they infiltrate to the groundwater depends on transformation in the root, vadose and saturated zones by microbial or chemical actions. The risk to groundwater quality is determined by: - the depth to water table, flow characteristics through the soil, and water management practices used by the agricultural system.

The presence of nitrogenous fertilizers can in certain circumstances, encourage the translocation and persistence of some biocides. For example, in low-nitrogen, lateritic soils in India, the addition of ammonium sulphate and urea reduced the rate of degradation of carbaryl and carbofuran (Rajagopal, 1984).

### *Sandy soils*

Soils which have high hydraulic conductivity and low attenuation capacity are particularly prone to permitting stable biocides to translocate through the vadose zone (Mossbarger, 1989). Commonly, the vadose zone contains less clay minerals and organic matter than the root zone, which means that if biocides reach the vadose zone there is less particle surface on which they can be absorbed and thus their persistence and mobility tend to be greater.

### *Structured soils*

Even in an idealised soil profile, the translocation rate for most biocides is slow, only the most mobile substances would travel faster than say 1m per year. However in real situations, preferential flows may develop in the unsaturated zone below relatively impermeable surface horizons. Where these flows develop, the rate of transport of biocides to the underlying water-table may be many times more rapid, since there is far less opportunity for retardation by molecular diffusion, adsorption, chemical reaction and microbial degradation.

### *Silt-loam soils*

Certain biocides applied to the surface of silt-loam soils, have appeared in drain outflows in relatively short periods - for example in as little as four days (Kladivko, 1991). These biocides behave similarly to nitrates and permeate the soil relatively easily. For example, atrazine has been found in groundwater aquifers under many agricultural systems, and is regarded as a biocide which is particularly liable to reach groundwaters (Exner, 1990).

The magnitude of leaching effectiveness is greater for basin irrigation than for sprinkler irrigation. Furrow irrigation has the highest leaching effectiveness. This can be attributed to the shallower wetting depth achieved under sprinkler irrigation (Troiano, 1993). The method of water application, as well as the amount of irrigation water added, determine pesticide movement, and are important aspects to consider in the management of pesticides.

### Contamination of aquifers from surface waters

Penetration of biocides from affected surface water channels to shallow groundwaters has recently been recognised as a significant consequence of agrochemical activities. Recent results (Blum, 1993) have shown that it has taken place even in environmentally aware countries such as USA. It is of particular significance when the receiving groundwaters are used for municipal water supply, because the biocides are hard to detect, have profound effects and are difficult to remove.

Measurements from the USA on the movement of biocides from surface water to shallow groundwater aquifers, showed that river water contaminated with Atrazine affected wells within three metres of the bank in about 21 days. The biocide was in fully dissolved form (Blum, 1993). This translocation rate was substantially faster than that suggested for diffusion by numerical modelling (the standard matrix transport model) and implies that preferential horizontal flows occurred in the soil at, or just below, the water table.

### Direct contamination of surface waters

Shortcomings of pesticide operators are a significant and unquantifiable factor in pesticide pollution in surface waters (and associated recharge to groundwaters). The major causes are:-

- (i) improper cleaning or disposal of containers,
- (ii) mixing and loading of pesticides in an area where residues or run-off are likely to threaten surface or ground water.

### Vapour drift

Surface water can be affected directly by the travel and deposition of fine pesticide droplets when pesticide spray is applied too close to water bodies. Drift incidents can result in greater surface water contamination than either runoff or leaching. Rainfall can absorb pesticide and will deposit it wherever it lands - on soil

plants or water bodies. The pesticide it absorbs can be vapour drift or can even be pesticide vapour rising from above areas where applications have recently been made.

#### Soil leaching characteristics

Large soil pores (macropores, worm-holes, root-holes) have a significant effect on solute transport (Beven, 1982). In an unsaturated soil matrix, free water can move down through large pores, such as cracks in a clay soil. In a clay soil, the addition of water (through irrigation or rainfall) results in the wetting up and swelling of the soil columns and closure of the macropores between them. Thus if biocide (or fertilizer) is applied first, then the subsequent irrigation will leach it relatively rapidly. If, however, it is applied second, (i.e. the soil has already been wetted) the macropores will have closed up and biocide leaching rate will be minimised.

#### Biocide leaching characteristics

The degree to which any biocide can be leached is dependent on :-

- (i) the nature of the soil with respect to adsorption and permeability (biocides tend to leach less in clay soils than sandy ones),
- (ii) the ability of biocides to bind to the soil particles,
- (iii) the biocide's persistence in the soil,
- (iv) the biocide's solubility,
- (v) the amount of leaching water and the rate of application.

## **6. EFFECTS OF AGROCHEMICAL POLLUTION**

### **6.1 Health effects of agrochemical pollution**

This section describes the different effects of agrochemical (1) on human health, and (2) on the local environment in terms of both surface and groundwater. Groundwater accounts for almost 100% of water supply sources for populations in developing countries. In developing countries, polluted water may contribute to 80% of diseases (Vrba, 1986).

#### **6.1.1 Nitrates**

The main danger from nitrate is perceived to be methaemoglobinaemia ('Blue Baby Disease'), which causes haemoglobin in the blood of infants to be converted to a form which cannot carry oxygen (methaemoglobin). When around 15% of the blood haemoglobin is affected, it causes a blue discoloration of the skin. Approaching 50% it causes shortness of breath and a fast heart rate (Le Fanu, 1994), and may cause death through asphyxiation. Infants up to 4-6 months of age are particularly susceptible because of the lack of acidity in their stomachs and the possibility of gastrointestinal infection, which would allow nitrogen-converting bacteria to flourish (Klassen, 1986; Wetzlich, 1991). It is emphasised that these conditions only develop when nitrate concentrations in drinking water approach 15,000mg/l. This concentration is 300 times the present recommended permissible level.

Nitrate is also indirectly implicated with cancer due to its conversion to nitrite by bacteria as described below.

#### **6.1.2 Nitrites**

Nitrites can also react with naturally occurring functional groups in the foods called secondary amines, forming a class of chemicals called nitrosamines (Menzer, 1991). At very high doses, these cause liver and lung damage, convulsions, birth defects, and cancer (National Research Council, 1981; USEPA, 1987b).

The presence of nitrates and nitrites has been linked with cancer (Bockman, 1991), but this view is still contentious (Conway, 1991). Nitrate is converted to nitrite by bacteria, which is followed by the combination of the nitrite with amines and amides, which are normally derived from food, to produce N-nitroso compounds, such as nitrosamines and nitrodamides. These are known to be powerful

carcinogens in a wide variety of animal species (Maagee, 1967). An epidemiological link has not been established yet, but high incidence levels (at 150 per 100,000 population) of gastric cancer have been noted (Cuello, 1976) in the Colombian Andes where there is a high concentration of nitrate in drinking water supplies.

The WHO are proposing guideline of 3mg/l for nitrite (WHO, 1993) in drinking water. At a pragmatic level, this has to take into account the possibility of nitrate also being present above or below its own guideline.

### **6.1.3 Phosphates**

Few, if any adverse human health effects have been linked to exposure to high levels of water-borne phosphates (Klaassen, 1986). The EU recommend a maximum allowable concentration of 5mg/l (Chapman, 1996) but there appear to be no comparable guidelines from WHO or the USA. Phosphates are an essential nutrient and are readily taken up by plants, they are thus very unlikely to rise to high concentrations (Chapman, 1996). If high concentrations are found, they are likely to indicate a specific pollution problem.

### **6.1.4 Biocides**

Biocides can pose a serious hazard to all forms of life including humans. They have a high affinity for lipids in biological tissues. Even when they are only present in run-off in trace concentrations, bioaccumulation processes may result in high and even lethal concentrations in the tissues of higher predators, including man (Hindin, 1970). Many biocides are capable of affecting a wide range of non-target species.

WHO reports that 500,000 people are poisoned by biocides each year, of whom at least 5,000 die. The biocide poisoning rate is 13 times higher in developing countries than in the United States (Wier, 1981).

#### Herbicides

Urea derivatives and herbicides such as 2,4-D, 2,4-DP, 2,4,5-T, MCPA and dicamba are skin and mucus membrane irritants. 2,4,5-T is associated with a skin condition called chloracne. Nitroamatic herbicides (e.g.. dinitrophenol, dinoseb, dinitrcresol formulations) affect cellular metabolism and have been associated with hyperthermia, rapid breathing, dehydration, liver & kidney degeneration (Morgan, 1989).

#### Insecticides

Both organophosphates (phorate, disulfoton, parathion, fonofos, dichlorvos, acephate, malathion and diazinon) and carbamates (aldicarb, oxamyl, carbofuran and carbaryl) can be extremely toxic because of their ability to interact with the enzyme acetylcholinesterase. This enzyme is necessary for the normal functioning of the nervous system.

#### Fungicides

A number of older fungicides are associated with respiratory and dermal irritation (Morgan, 1989). But most of the recently developed fungicides (i.e.. systemics, sterol-inhibitors, benzimidazoles etc.) are specific for certain plant pathogens and have little effect on animal species.

## **6.2 Environmental effects of agrochemical pollution**

### **6.2.1 Nitrates**

The addition of fertilizers from drainage flows, contributes to the process of eutrophication in receiving surface waters. This inevitably effects the balance between the growth of organic matter in the lake and the availability of nutrients. Algae in nutrient rich waters utilise the extra nitrates to multiply up to a dense population. As the algal population expands, it suddenly depletes the available oxygen supply in the water

and may cause fish kills or impairment of fish species. Large scale blooms of algae may cause further problems by releasing toxins themselves to prevent other species of algae thriving.

### 6.2.2 Phosphates

Phosphates also contribute to eutrophication, in their role as an essential nutrient. The extent of eutrophication is usually controlled by the amount of phosphate not nitrogen, phosphate being the limiting nutrient. The uptake of phosphates by organisms in the water leads to the release of more adsorbed phosphorus from sediments forming a feedback mechanism which can exacerbate the problem (Klaassen, 1986).

### 6.2.3 Biocides

Penetration of biocides through to downstream surface waters at significant levels may lead to disruption to both flora and fauna ecosystems - depending on the type of biocide involved. However the fraction of applied biocide that is lost in drainage water is very low (Wauchope, 1978), rarely exceeding 0.5%. Some biocides, notably organochlorines, arsenic and paraquat, are strongly adsorbed to soil particles and will only reach the drainage water if the soil itself is eroded. Some herbicides, such as wetted powders, are far more soluble and can lose up to 5% (Conway, 1991).

The main impacts of biocides penetrating water sources are described in the sections below:-

#### Bioaccumulation

Some agrochemicals can bioaccumulate in edible organisms and make them unsafe for human consumption. Guidelines on admissible intake rates have been defined by the FAO/WHO Group of Experts on Pesticides.

#### Contamination of drinking water

Widespread contamination of drinking water, particularly groundwater, has been detected in Europe, due especially to the over-application of herbicides (Calamari, 1993). Contamination of groundwater by biocides was previously felt to be insignificant, but following documented problems, it is now a major concern. The problem is that if and when they reach the groundwater they are then unlikely to degrade at a significant rate and will therefore, without treatment, be present continuously in derived drinking water (Fawell, 1991).

#### Vapour drift

During the application of pesticides there is considerable scope for the applied pesticide to miss its target and to drift to neighbouring areas where, depending on the nature of the applied biocide, it may have adverse effects. Additionally, there may be further losses immediately after application due to the biocide evaporating from the soil. The rate depends on the volatility and reactivity of the biocide and on the nature of the soil.

#### Effects on microbiota and algae

In water, concentrations of carbofuran below 1mg/l appear to stimulate the growth of green algae. Growth is progressively inhibited by higher concentrations, and stops completely above 750mg/l.

In surface waters, biocides have been found to be toxic to bacteria which oxidise sewerage wastes. The LD<sub>50</sub> for Dursban and Naled is around 200-280mg/l (Steelman, 1967), whilst Baygon and Malathion were the least toxic with LD<sub>50</sub>s at around 6000 to 9000mg/l. It was concluded that levels of around 1mg/l would not cause appreciable inhibition of normal sewerage degradation processes. In general, these toxic levels are far higher than will be likely to develop even in the most severely contaminated agricultural run-off or drainage.

### Effects on fish

In fish toxicology it is common practice to refer to the standard lethal dose of a toxic materials as the LC<sub>50</sub> - that is, the concentration which kills half the fish in a specified time. The LC<sub>50</sub> is not equivalent to the LD<sub>50</sub> statistic, since the later refers to a dosage of toxic material which is generally administered in food or by injection.

However, for practical comparisons, the LC<sub>50</sub> statistic is very useful. The importance of even low concentrations of biocides - and especially those persistent types such as DDT which have a low water solubility - has often been emphasised. The capacity for living organisms to build up heavy body burdens through the process of bioaccumulation of these substances through the food chain is an extremely important environmental hazard which the LC<sub>50</sub> data for individual species may not reveal.

In the USA, trout which accumulated DDT in their ovaries at around 4mg/kg wet weight were sterile. The need to restrict the use of substances such as DDT just to functions for which no other viable treatment exists has been strongly stated (Butler, 1970).

Similarly, lindane ( $\gamma$ -HCH) at environmental concentrations as low as 10 $\mu$ g/l is not considered to be safe. Estuarine fish exposed over an extended period to levels such as 21 $\mu$ g/l showed negligible growth and increased mortality rates due to bioaccumulation of the biocide in their tissues (Bakthavathsalam, 1981). Mercury-based fungicides are also dangerous to fish. Even very low levels of exposure have been found to inhibit ovarian development in catfish in India (Kirubagaran, 1988).

## **7. PERMITTED CONCENTRATIONS**

Permitted concentrations of various nutrients and biocides have been set by various national, regional and international bodies based on various experimental methodologies and risk and uncertainty perceptions. The lack of a consistent formulation of standards, as demonstrated in the following sub-sections, leads to problems of differing standards which makes it difficult to compare the severity of problems between regions and the magnitude of the actual problem. This lack of problem definition can lead to mis-allocation of resources including grants, aid and research and to unrealistic risk predictions.

### **7.1 Nutrients**

#### *7.1.1 Nitrates*

There is quite wide disparity in water quality standards which have been claimed to provide 'safe exposure levels' for human health. This complicates the issue of assessing what are the actual risks of nitrates to public health. For example, the European Community required all drinking water supplies to have less than 50mg/l of nitrate by July 1994 (WHO, 1989), and the present guideline level of 25mg/l will eventually be adopted as the maximum acceptable concentration (MAC) for nitrate throughout the EC. Reducing the MAC for nitrate to this level has enormous cost implications for the water supply industry.

The World Health Organisation (WHO) considers 50mg/l to be the safe upper limit for nitrates in drinking water. Concern has been expressed that rising groundwater nitrate levels will reach the 50 mg/l level in shallow aquifers underlying Alsace, France, by around the year 2040 (Ramon, 1987).

The US EPA standard 'maximal contaminant level' (MCL) is 10mg/l (Bouchard, 1992) of nitrate nitrogen, which is equivalent to 45mg/l of nitrate. Workers at the US Department of Agriculture have regarded levels as low as 4.6mg/l as 'elevated' concentrations, and only when levels fell as low as 1mg/l or less were they regarded as unremarkable (Hubbard, 1989). However, these reports referred to nitrate nitrogen, for which the equivalent nitrate levels would have been 20mg/l and 4.5mg/l as nitrate respectively. In Canada, nitrate levels above 1 mg/l have been considered to be worthy of note (O'Neill, 1993).

The variation in standards means for example, water supplies in India which contain around 15mg/l of nitrate would be considered acceptable by WHO, the latest EC opinion, and the US EPA, but not acceptable by the US Dept of Agriculture and Canadian authorities. Different criteria seem to have been adopted by different organisations in India to judge nitrate contamination - varying from 20mg/l to 45 mg/l.

The widespread occurrence in India of groundwater with elevated nitrate has been linked directly with increased nitrate use in agriculture by many workers. It is significant that a recent study in India showed that, even in areas in which groundwater concentrations of nitrate exceeded 1000mg/l, no confirmed diagnosis of nitrate poisoning in the vicinity appears to have been made (Saxena, 1991). It would appear that there is a need for clarification on the level at which nitrate in groundwater poses an actual, rather than a perceived, threat.

In discussion about safe nitrate levels it is appropriate to point out that the agricultural guidelines are quite similar to public health ones. FAO recommends an upper limit of 30 mg/l for irrigation water (Basile, 1991), and in Thailand a maximum level of nitrate of 10 mg/l may have been recommended in order to prevent damage to ripening rice (Sato, 1988).

### 7.1.2 Phosphates

No drinking water standards have been established for phosphates (USEPA, 1989, 1990).

## 7.2 Biocides

A full list of the uses of different biocides is given in Appendix I. The list also includes details of some of their physical characteristics.

The 1991 European Community Pesticide Ordinance set a Maximum Admissible Concentration (MAC) for any single pesticide in drinking water of 0.1 µg/l. This MAC is widely viewed to be extremely demanding, and reflects the requirement that these toxic compounds should not be allowed to spread from the place of application rather than to meet any specific physiologically tolerable level. One outcome is that the limit is commonly exceeded in many EC public groundwater supplies.

The European Commission set MACs for biocides in drinking water, which came into effect in 1985. These MACs were adopted in Britain in 1989 and comprise 0.1µg/l for any one pesticide, and 0.5µg/l for total pesticides.

The Commission has also set Maximum Residue Limits (MRLs) in fruits and vegetables for over 40 pesticides. In the USA, Threshold Limit Values (TLVs) for pesticides were set over 30 years ago, with no clear method of assessment. The US National Academy of Sciences has estimated that the US Authorities hold adequate safety data on only 10% of pesticides, incomplete data on 52%, and none at all for 38%. The US Environmental Protection Agency (EPA) has found that nearly 70 out of 300 pesticides approved before 1972 cause cancer in animals. They also found that in recent years uncertainty in the regulation process has led to confusion amongst users and regulators.

There is a well established approach for toxicology evaluation of pesticides which has been developed over the last few decades. An extensive programme of acute and chronic toxicity studies in laboratory animals are conducted to identify immediate and long-term effects to assess potential implications for human health. The potential for neurotoxicity, teratogenicity, mutagenicity, and carcinogenicity are evaluated in the programmes. A major outcome of this research is the establishment of the dose level at which no toxicological effect has occurred (No Observable Adverse Effect Level - NOAEL) from which a safe level in man is extrapolated., by application of an appropriate safety factor of at least 100. From this, it is possible to calculate the amount of pesticide that can be harmlessly consumed per person per day. This is the definition of the 'Acceptable Daily Intake' (ADI) for man expressed as mg per Kg of body weight per day. The ADI is the basis used by regulatory authorities and international organisations (WHO/FAO) in



their evaluation of the safety of pesticide residues in foodstuffs (Roberts, 1988). Maximum residue limits (MRLs) are used for pesticides on raw agricultural commodities and are nothing to do with toxicology

The WHO has laid down principles for setting Drinking Water Guideline (DWGL) Values for organic chemicals (Roberts, 1988) using an approach where a fraction of the ADI for a particular pesticide is applied to drinking water. If an ADI had not been established then a 100x safety factor should be applied to the NOAEL. With most compounds, 10% of ADI is taken. The USEPA have adopted a similar approach except that 20% of the ADI is used and the resulting figure is termed a Health Advisory amount (rather than a DWGL) for lifetime exposure (see Table 5 for full USEPA list).

#### *Hazardous pesticide list*

A list of particularly hazardous pesticides was established in 1985 as part of lobbying for strict controls, bans, and ultimately elimination. The list, called the Dirty Dozen, was based on criteria that included: hazards to human or environmental health, evidence of widespread use and resulting harm, bans in exporting countries. The list of pesticides are banned in many countries, yet many are still promoted and used, especially in developing countries, where weak controls and dangerous working conditions make their impact even more serious.

There are in fact 18 chemicals on the list. There would be more, but several can be grouped together because of their closely related chemical structure.

Aldicarb (Temik)	DDT	Lindane
Camphechlor (Toxaphene)	Aldrin	Paraquat
Chlordane	Dieldrin	Parathion
Heptachlor	Endrin	Methyl Parathion
Chlordimeform	EDB	Pentachlorophenol
DBCP	HCH/BHC	2,4,5-T

#### *Persistent Organic Pollutants*

Initiatives to put the list of hazardous agrochemicals into a more formal structure, have resulted in a draft protocol for Persistent Organic Pollutants (Ongley, 1996). This list includes other checks, such as PCBs and heavy metal compounds. Since many are agricultural pesticides, some of which are still widely available in developing countries, there will be a number of hurdles for the agricultural sector to cross such as :- (i) development of safe alternatives, (ii) realistic regulations and (iii) effective enforcement.

Methyl bromide is also a hazardous biocide, but in respect to its effect on global atmospheric ozone depletion. It is estimated that methyl bromide is responsible for 5-10% of ozone depletion, mainly due to its use in USA.

## **8. ASSESSMENT OF RISK OF POLLUTION**

Infiltration rate, water table depth and volume of water have an effect on the time it takes for agrochemicals such as nitrates to penetrate the unsaturated layer and reach aquifers, and for nitrate concentrations in aquifers to rise in response to increased nitrogen fertiliser application rates at the surface. In drier climates, the leaching of nitrates can be delayed from season to season until there is a net downward flow through the vadose zone. The time at which the greatest amounts of nitrates are transferred to surface and groundwater is closely related to rainfall and water application patterns.

When observing the process of agrochemical (nitrate) leaching, the following factors play a primary role (Funari, 1991):-

- Textural, mineralogical, microbiological, and physio-chemical properties of top soil
- Hydraulic properties (mainly permeability) of soil layers between the surface and water table which control the downward percolation of contaminating fluxes

- Thickness of the unsaturated zone
- Availability of infiltrating water, which is the main carrier for the transport of polluting substances downward to groundwater

The most vulnerable situations are those where there are highly permeable soils which permit a high rate of infiltration and have no intermediate impermeable layer before reaching the groundwater.

Soil texture affects leaching. Soils that have smaller, flatter particles such as clay have more surface area and chemical charge than soils with less surface area such as sand. Fine clay has about 10,000 times more surface area as the same weight of medium sized sand. Pesticides and fertilizers tend to bind or adsorb to the larger surface area as there is more surface area for adsorption. Thus, very sandy soils are likely to have more potential for leaching.

Vulnerability of groundwater to pollution may be defined by means of the capability of contaminating substances to penetrate into the water body, preventing its potable use. This depends on:-

- physical & climatic conditions of the site
- hydrogeological properties of the vadose zone & aquifer
- physico-chemical properties of the agrochemicals

The vulnerability of groundwater to pesticide residues depends on the ratio of their persistence and residence time in the overlying soil. A compound of high enough persistence will reach the groundwater table in the long run, even if it has a long residence time in the soil. Examples are chlorinated carbons with low volatility like endrin, dieldrin, and DDE (Loch). Soil type also plays an important part since its metabolic activity will affect biocide leaching, i.e. a high nutrient level and supply of fresh organic matter will favour biological activity. The organic matter content and thickness of the humic soil horizons also effect the residence time of compounds in the soil. For weakly acid compounds pH also has a strong influence, permitting higher mobility of compounds as it becomes more alkaline.

Underlying groundwaters are vulnerable to contamination by pesticides where the soils are sandy and have low organic matter, e.g.. arenosols, gleysols and podzols. Soils of high organic matter content like; histosols, fimic anthrosols, chernozems, etc tend to accumulate pesticides, especially persistent residues.(Loch, 1991).

## **8.1 Assessment of risk from particular biocides**

### *8.1.1 Health Risk*

In assessing the risk to human health from a particular biocide two factors are principally considered.

The first factor is simply to determine the likely exposure' of people to the biocide. This can be done in terms of the concentration at which the biocide is occurring (in say the water supply or in certain foods) and the length of time (days, months) that people are subjected to it.

The second factor is the toxicity of the particular biocide, or how hazardous it is. This factor is determined using "indicator" species - a series of plant and animal species for ecosystems and other mammals for humans. The indicator species are exposed to the chemicals in air, food and/or water over a range of concentrations, and the toxicity of the chemical at each concentration is observed. Both acute (short-term, high exposure) and chronic (long-term, low exposure) studies are conducted. Since individual members of a test species exhibit a range of sensitivities to chemicals, in most experiments a "median lethal concentration" is determined or  $LC_{50}$ , the concentration that is lethal to half the test population. The more hazardous the chemical, the smaller the  $LC_{50}$  and the smaller the amount to be toxic. Since humans may be more sensitive than the test species, a safety factor ranging from 1/10 to 1/1000 is used. "No-effect" levels

for long-term exposures and effects such as birth defects and cancer are more difficult to estimate, and safety factors are increased.

The resulting levels of concern are compared to measured or predicted pesticide concentrations in water and food likely to occur in the environment when the pesticide is used. If estimated environmental concentrations (EECs) for aquatic ecosystems exceed half LC<sub>50</sub> for the most sensitive test species, then risk is of high concern. If EEC is more than one-tenth LC<sub>50</sub> restricted use is considered. If EEC is less than one-tenth LC<sub>50</sub> risk is considered small (Wauchope, 1994).

The risk associated with each biocide can be expressed in terms of the ADI and NOAEL (as discussed in Section 7) and takes into account a sizeable safety factor of 100. ADIs have been established for a range of pesticides by the USEPA and the WHO and are well defined. The tables given in Section 7 give a frame of reference to which health risk can be related.

### 8.1.2 Environmental risk

In assessing the risk from particular biocides to the environment, two approaches are widely used. The first is to assess the environmental fate in soil and water. This involves targeted studies that enable the stability and persistence of the biocide to be determined as well as the nature of any degradation products.

The second is the toxicology, i.e. the hazard posed to the environment by a particular compound. This is the same approach as above but applied in consideration of bioaccumulation of toxic compounds in ecological food chains, rather than as an indicator of likely toxicity to humans.

A simple procedure has been developed (Calamari, 1992) to enable preliminary hazard assessment to be carried out on a small-scale. The assessment gives a 1, 2 or 3 rating to five categories and then derives an overall comparative index by multiplying the five indices together. The indices are based on the five main assessment categories:-

	1	2	3
Toxicity (fish) mg/l LC <sub>50</sub>	>10mg/l	0.1-10	<0.1
Persistence time	days	weeks	months
Bioaccumulation log K <sub>ow</sub>	<3	3.-3.5	>3.5
Leachability	<1.8	1.8-2.8	>2.8
Volatility log (V <sub>p</sub> [MW] <sup>2</sup> )	<3	3-0	>0

LC<sub>50</sub> = Lethal concentration for 50% population

K<sub>ow</sub> = octanal B water partition coefficient

GUS = Groundwater Ubiquity Score

V<sub>p</sub> = Vapour pressure

MW = Molecular Weight

More refined assessments should then be carried out on the one or two chemicals found to be most likely to be hazardous.

## 8.2 Assessment of risk to a particular location

Before commencing assessment it is necessary to first identify the perspective of the location (Rickert, 1992) and to evaluate whether it is representative of a national situation, a regional situation, a catchment situation or a specific project area. This makes a lot of difference to the amount and number of types of information that may be sought.

At whichever level is required, information will initially need to be collected based in terms of:-

1. A clear understanding of the hydrological framework

2. A search and analysis of existing data
3. Initial evaluation of existing surface water parameters

Based on this information, the main programme to collect information can then be planned. According to specific requirements it will either utilise fixed regular water samplings or detailed sampling to gain data on focused objectives.

The results of detailed investigations can be utilised either to determine directly the sources/causes of agrochemical pollution problems or to develop a mathematical model that can be used to test pollution causes and to evaluate alternative management strategies.

Detailed investigations of agriculturally related water quality problems (Rickert, 1993) should cover the following elements:-

1. Potential source/cause of problem
2. Quantification of the problem
3. Define the objective of the investigation
4. Define the geographical area of interest
5. Define the timing and duration of any sampling
6. Define the sampling sites
7. Describe the approach used
8. Describe how the data will be analysed and used
9. Provide results and conclusions

### **8.3 Assessment of present agrochemical usage**

Agrochemical use survey involves collecting information on: (i) type of crops grown, (ii) relative cropped areas, (iii) area under irrigation, (iv) type and amount of agrochemicals used, and (v) official guidelines on addition rates. The survey is conducted through interviews with government officials, agrochemical retailers and the farmers themselves. It can be quite revealing to examine how large a difference there is between the amount of agrochemical recommended for an area the amount of agrochemicals apparently being distributed to farmers and the amount farmers assess that they themselves are using.

A recent study in the Gujarat region of north-west India (HR Wallingford, 1995), found that actual use of agrochemicals was much lower than recommendations. This was attributed to farmers' reluctance to overspend when planting the trees. However the retailers had a different view to the farmers on how much agrochemical was being used. In some respects this is indicative that farmers would be receptive to new low application techniques such as IPM (Integrated Pest Management).

### **8.4 Assessment of existing agrochemical pollution situation**

The first step of this assessment would be to acquire information on present cropping patterns and to identify if possible, any regionalisation of crop-types. The next step would be to identify a representative or a groundwater sampling well, in each of these areas, and commence with regular sampling (weekly, fortnightly or monthly) to monitor agrochemical pollution patterns. This should be tied in with consideration of cropping schedules (when do farmers apply biocides) and the types of biocides they use as well as climatic factors (e.g. run off following monsoon heavy rainfall). Figure 8 gives a representation of cropping patterns in an Indian irrigation system recently investigated. Monitoring of drainage flows in main drains emanating from the cropping areas identified monsoonal peaks in biocide runoff. Samples are analysed in a suitable laboratory for suspended pollutants. The water should be filtered or centrifuged to separate out suspended sediment. The analysis should quantify pollution levels in both the water (soluble pollutants) and the sediment (adsorbed pollutants).

## 8.5 Assessment of potential pollution by predictive techniques

Computer simulation models can be used to analyse the effects of different agricultural and irrigation management options on non-point pollution of water bodies. There are many models (see Table 6) and they range from simple procedures to sophisticated one-dimensional and two-dimensional simulations that can include algorithms representing complex physical processes.

The most important step is to select the right model for the simulation of a particular situation. It is a task for the specialist to ensure that the right model is utilised, and that the complicated procedures involved in it – utilising and ordering data and interpreting results – are carried out reliably. For the project manager the task is much simpler – identify the area, identify the most likely suitable crops and then allow the specialists to predict the extent of environmental and public health risk created.

### 8.5.1 Review of existing models

The main objective in carrying out any model study is to predict the extent of agrochemical pollution that will result from growing a certain crop on a certain soil, under a given irrigation/rainfall schedule for a range of different nutrients and biocides. Different types of model are used to predict run-off characteristics, sub-surface drainage characteristics and groundwater leaching characteristics. Furthermore different types of model may be needed in order to cope with the data that is available. Complex distributed models generally require detailed intensive data taking into account spatial variations in model parameters. Simpler models that assume spatial homogeneity and take account of fewer processes can be used far more cheaply since they require much less data and are much quicker to set up and to run, though they are often more site specific.

The wide range of models available is listed in Table 6, and an outline of their purpose is given. Some models are very sophisticated and can be applied to a wide range of situations, including the particular requirements of agrochemical management in arid and semi-arid regions. However they are also very demanding on required input data, and for this reason may be difficult to apply.

Furthermore many of the basic relationships especially semi-empirical relationships and the processes given prominence are based on work carried out in developed countries where climate conditions and agricultural practice are quite different from those in most developing countries.

There is a strong and urgent requirement for the development of agrochemical fate models suitable for use in the field conditions found in developing countries.

### 8.5.2 Review of uncertainties in pollution prediction

Accurate prediction of the fate of agrochemicals is made difficult by the large variability in soils (and their properties) which give rise to numerous complex interacting processes that govern the transport of the agrochemicals (IUPAC, 1991).

In order to select a model that is appropriate in a given situation for assessing agrochemical distribution, the user needs to identify:- (i) the required outputs needed from the model study which will determine the model required, (ii) the desired accuracy, (iii) the resources available, (iv) how much is already known about the situation.

Comprehensive models can give relatively accurate estimates, but they require large amounts of data and are only as good as the input data available and the processes included. However, models can be useful in identifying dominant local mechanisms and constraints and provide information on worst case scenarios (IUPAC, 1991).

Models of agrochemical distribution in water bodies are far more accurate than those for soil since they are far more homogenous and, therefore, less site-specific.

## 8.6 Measurement of pollution levels

Direct measurement can be done in three ways:-

- (a) field measurement in a real situation,
- (b) laboratory measurement on samples taken back to the investigating organisation,
- (c) measurement under controlled field conditions – either replicate plots on a research farm or small lysimeter blocks.

The losses of nutrients and biocides added to productive areas can be measured in a number of ways, each having different assumptions and different sources of error.

### Soil sampling

Soil samples are taken at different depths. Large numbers of samples are required to obtain representative results. An alternative is to sample tile drains.

### Lysimeter

The use of a physical lysimeter is a more precise method. The lysimeter commonly consists of a block of soil isolated from the surrounding field by an impermeable material to prevent dispersion of water, with arrangements at the base for collecting the drainage water. The soil block complete with field crop growing on it, is then treated in exactly the same way as the rest of the field with rainfall, irrigation and additives, such as agrochemicals. Further lysimeters are used to assess alternative options, or conditions.

Lysimeters provide a means of studying the environmental fate of nitrates and pesticides. They provide valuable information, obtained under realistic field conditions, on metabolism in plants and soil, on mobility through the soil profile and on leaching below the depth of the soil profile (Yon, 1991).

Lysimeters can be filled with either disturbed soil or undisturbed soil. Filling a lysimeter with disturbed soil normally involves removing the soil from the site, layer by layer, and then placing the soil into the lysimeter so as to best represent the soil in its original state. The undisturbed technique requires that the lysimeter be filled with a soil monolith, which is removed intact from a suitable location.

In order to carry out a lysimeter study, it is necessary to know the following properties about the agrochemical to be tested. These comprise:

- physical properties e.g.. aqueous solubility
- sorption values in various soils
- rates of degradation
- metabolic pathways in soils and major soil metabolites
- information on other potentially significant loss mechanisms e.g.. volatilization
- analytical methods for quantification of chemical in water and soil

One practical point is that concentrations of the nitrate/biocide measured in the leachate have to be assumed to be representative of those levels which are typical for soil-pore water leaving the root zone of the soil.

### Core profiling

Sampling can be taken from deep cores sunk through the unsaturated and saturated zones above underground aquifers. These produce profiles of the pattern of downward movement of leachates.

### Surface water sampling

Water samples should be taken at the point of entry and exit to the project area. At the first stage of the monitoring programme, 3 or 4 samples should be taken depending on the width of the water source to check the heterogeneity, if the water is deep samples may also be taken at depth. If the pollutant cross-

section is uniform, future samples can be taken from the most convenient location, usually the bank. Care however must be taken that the uniformity is not effected by seasonal or flow changes where relevant.

#### Groundwater sampling

Initial testing of groundwater may be possible by hand-digging or auguring to a depth below the watertable, and collecting samples in glass bottles, this may be sufficient if the principle movement of agrochemicals is to nearby abstraction points due to the drawdown of groundwater levels (section 3.1.2). For abstraction of groundwater from shallow depths i.e. not more than 5-8m below the soil surface, horizontal methods (galleries) are recommended. For deeper abstractions the method will depend on aquifer properties and available resources a complete discussion being provided by Driscoll (1986). In sampling groundwater as with surface water seasonal variations need to be taken into account.

#### Analysis

The cost of sampling for the detection of biocides is not dissimilar to sampling for more easily assessed parameters such as nitrates, (Rickert, 1993). However the cost of analysis is very much higher. This is because of the sophisticated instruments needed to provide a comprehensive detection and measurement service. The instruments used are the Gas Chromatograph (GC) and the Mass Spectrophotometer (MS). Further costs are generated because of the need to retain high calibre technical staff and to maintain a sophisticated laboratory environment. The high costs of GC/MS analysis of biocides emphasises the need for the development of less costly tests for screening or for detecting presence.

Immunoassay tests have recently been developed that enable certain pesticides to be detected using simple test-tube/photometer technology that can even be carried out in the field (thereby avoiding inaccuracies due to degradation of the sample). The tests are based on biochemical splicing of biocide molecules with enzymes. This enables them to utilise immunoassay techniques that can give reliable indicative assessment at the very low trace concentrations at which pesticides are perceived to begin to cause problems.

## **9. MANAGEMENT OPTIONS**

Soil chemistry and the hydrological regime in the unsaturated zone have a large effect on nitrogen transformations in the soil and the transport of biocides and the resulting impacts on surface and groundwater reserves. Guidelines on Best Management Practices (BMPs) have been developed to minimise the risk of nutrient contamination of the water resource.

Recent EC Directives have been designed to promote the widespread adoption of BMPs to reduce the main mechanisms of loss of agricultural chemicals. It is recommended that BMPs should include “whole life-cycle design” so that potential agrochemical pollution of water is considered at the project design stage.

Best management practices may include:-

- (a) Humus is important in agricultural practices as it can substantially reduce the risks of nitrate losses to the groundwater by:-
  - (i) acting as a slow-release nitrogen source, which provides a source of carbon (required as an energy source) for denitrification bacteria (i.e.. acting as a chemical buffer)
  - (ii) acting as a physical ultrafiltration medium
  - (iii) providing a location for soil water storage.
- (b) Erosion and sediment losses can be controlled by the use of conservation tillage, run-off diversions, grassed waterways, filter strips, crop rotation and winter ground cover.

- (c) Pollution from animal feedlots and intensive grazing systems can be reduced by lowering livestock population densities and by sludge injection over larger land areas.
- (d) Elevated levels of nitrates and phosphates in waterways downstream of agricultural areas can be controlled to a certain extent by the use of artificial wetlands and by lateral reed buffer zones along the waterway.
- (e) Nitrogen and phosphorus losses can be reduced by testing soils for their nutrient levels, and only providing adequate amounts - preferably in slow release forms – when the risk of downward leaching can be minimised, especially where irrigation is employed.

A more detailed look at these additional practices are described in the sections below.

## **9.1 Soil management**

Management practices such as irrigation scheduling, fertilization based on calibrated soil tests, conservation tillage and acceptable cropping practices are highly effective in controlling the leaching of nitrates (Power, 1989). Once the processes of nitrogen transformation and transport have been understood, then potential methods for managing soil nutrients can be formulated so that leaching and run-off losses can be minimised.

### *9.1.1 Aeration*

Since many of the processes which affect nitrogen compound metabolism occur in the aerated root zone, it is very important to maintain adequate oxygenation in this zone. Conditions or activities which reduce aeration such as waterlogging or over-compaction, are likely to reduce nitrate availability to crop roots, and may allow ammonia to leach to the groundwater before it can be oxidised. (Norberg-King, 1993).

### *9.1.2 Choice of crop type*

The choice of the most appropriate type of crop for a specific irrigation site is an extremely important factor in reducing nitrogen losses to groundwater. Any vegetation which has a high nitrate demand, and is capable of absorbing it under the prevailing physio-chemical conditions, will help to reduce soil nitrate levels (Chakravarty, 1989). For example, in the USA, riparian zones consisting of buffer strips of permanent vegetation have been found effective in reducing nitrates in surface and near-surface run-off to drainage channels. Deeply rooted forest trees have been shown to be more effective in reducing nitrate levels in the soil above the water table than shallow rooted crops.

Adding fertiliser to plots with ground cover (especially leguminous herbs which are able to fix atmospheric nitrogen in their root nodules) has been found to significantly increase organic nitrogen supplies in the topsoil, which provide adequate nitrogen for subsequent growth after the tree canopy has closed above the plots (Machbub, 1988) .

In Alsace, France, the planting in winter season of green manure crops has been adopted to consume the residual nitrates left after summer harvesting of field crops, such crops are known as ‘catch’ crops. Also planting ground cover in vineyards has been found to reduce winter run-off of nitrate contaminated water (Ramon, 1987). Similarly, in the USA the planting of winter ground cover to reduce leaching during the non-growing season has been considered as an alternative nitrate-control strategy (Ritter, 1989).

Some crops are recognised as being associated with high levels of percolation of nitrate contained in water. In Luxembourg, it has been recommended that the cultivation of maize and potatoes should be avoided, in order to prevent excessive nitrate levels in aquifers.



### 9.1.3 Chemical modification

The use of nitrification inhibitors to reduce nitrate formation after the application of urea fertilisers has proved to only have a limited effect, mainly in the topmost layers of the soil, where ammonia and nitrite dominate. Nitrate formation tends to increase below about one metre. Soil nitrogen modifiers appear to be of restricted value in reducing nitrate losses in soils in which deeper percolation pathways become established, although they may be of value where the root zone can be effectively isolated from the groundwater for the relevant part of the growing season.

## 9.2 Nitrate Control Zones

The adoption of nitrate control zones is now a requirement of EC legislation. Farming practices have been brought in, which aim to protect water supplies which are required for storage reservoirs and wells, from excessive accumulations of nitrates (d'Orval, 1982). Bans on nitrate usage need to recognise the dynamic nature of nitrogen metabolism and the seasonality of risks, particularly those related to infiltration and run-off.

## 9.3 Improved nitrate application

### 9.3.1 Animal stock limitation

The contribution of intensive livestock rearing and, especially, livestock feedlots to nitrate pollution of ground-waters is now more widely recognised (Turner, 1979; Spalding, 1988). Poultry manure has been found to contribute more to nitrate contamination of groundwater than inorganic fertilisers. The limitation of livestock densities, especially on open soils with rapid percolation rates and low organic content, is seen as a prudent measure to combat groundwater contamination.

### 9.3.2 Fertiliser application method

Many methods/practices are available for applying fertilizer to land:

- (a) The amount of nitrogen fertiliser applied to land should take into account the residual levels of nitrogen in the soil (Ferguson, 1990).
- (b) Nitrogen loss through surface run-off can be at least partially reduced by the injection of slurry (semi-liquid animal manure) (Kofoed, 1981).
- (c) Growing green manures to take up surplus nitrates after crops have been harvested converts organic nitrogen into less soluble in organic forms, which act as slow release fertilisers in the following year (Ramon, 1987).
- (d) In rice fields, applying nitrogen fertilisers on top of standing water and allowing them to infiltrate into the paddy for five days without either further irrigation or drainage has been found to produce the lowest nitrate losses in the run-off to drainage (Singh, 1979).
- (e) The role of nitrogen-fixing Cyanobacteria ('blue-green algae') in providing supplementary nitrogen in rice fields and seasonally flooded fields in flood plains such as those in Bangladesh and Pakistan is now becoming recognised (Cross, 1992).

### 9.3.3 Timing of fertiliser applications

The time at which nitrogen is applied to crops has a significant influence on nitrate uptake. Isotope analyses have shown that there is a higher utilisation of fertiliser (inorganic and urea) nitrogen when application is delayed, because uptake and translocation within the plant is greater during the period when the seed is filling. However, levels of residual nitrogen in the soil may be higher after grain filling, suggesting a potential risk to groundwater if ground cover cropping does not follow grain harvest (Bigeriego, 1979).

Scheduling irrigation application in strict response to soil water depletion in order to reduce deep percolation has also been recommended in the USA, coupled with reduction of pre-planting application to avoid early leaching (Hergert, 1986).

In the UK, nitrate sensitive areas have been designated in response to an EC Directive requiring member nations to designate all zones vulnerable to nitrate pollution. In these zones, nitrate fertiliser should not be applied between mid-September and mid-February, since during this period there is a net downward movement of water which can carry nitrate through the soil to the underlying aquifers.

#### **9.4 Lateral drainage options**

The establishment of lateral drainage systems has been found to reduce the risks of groundwater contamination by both nutrients and biocides. In freely-draining watersheds in Britain, sub-surface run-off removes almost 80% of the available nitrate during the wetter part of the year. Obviously, the closer the spacing of sub-surface drains, then the more effective they are at removing nutrients and biocides from root zones.

Some mitigation measures for use for individual pesticides include:

- reductions in maximum recommended application rates or in the number of applications per season
- elimination of specific high-rate, high-risk uses
- reclassification of pesticides into the "restricted use" category
- buffer zones between application areas and water bodies and wells
- user (farmer) education about safe application technology and timing
- banding and other methods of more efficiently targeting pesticide sprays
- definition and protection of sensitive ecosystems and water resources
- pairing of soils having high leaching or runoff potential with pesticides having low leaching or runoff potential
- adoption of soil conservation practices that can decrease pesticide runoff in some cases

#### **9.5 Water table management**

Controlled drainage and irrigation can provide a means to control the groundwater levels where levels are relatively shallow. This can mean that when heavy rains are expected groundwater levels can be lowered thus increasing storage within the soil and thus decreasing runoff and thus potential agrochemical pollution to surface waters. At other times when pesticides and nutrients are already at high levels within the soil the groundwater level can be kept just below the root zone retarding leaching and keeping the agrochemical in the biologically active root zone longer for utilisation or degradation. Research published on the internet by US Department of Agriculture show reductions in losses of the agrochemicals atrazine and metolachlor by between 10-15% and from studies at North Carolina State University (R. Evans) of 50% for nutrients. The method may require sophisticated drainage control structures and reliable rainfall predictions to be effective.

#### **9.6 Fertilizer application under irrigation**

Applying a portion of a crop's nitrogen (N) requirement with irrigation water is a recognised best management practice to reduce nitrate leaching losses from some crops grown on coarse textured soils. Research in Minnesota has shown that splitting N applications on high N use irrigated crops such as maize, sweet corn and potatoes grown on sandy soils generally benefits crop yield, N use efficiency and associated environmental impacts (MES, 1993). The process is known as fertigation and it also enables frequent applications with minimal management and costs as long as when fertilisation takes place irrigation was also needed.

Irrigation should always be limited to wetting only the root zone, because excessive irrigation can transport nutrients below the root zone through leaching. Proper scheduling and uniform water distribution are necessary to assure control. Overhead and trickle irrigation systems require careful scheduling because it is difficult to detect over-irrigation by these methods, whereas seepage and furrow over-irrigation is visually obvious in overflow and ponding. Also biocides and nutrients are more diluted in irrigation water

(fertiligation or pestigation) than in conventional sprays, and there is less drift from sprinklers than from sprayers.

Fertilizer programmes are introduced to achieve minimum application for highest yield and considers the method by which fertilizer is applied, its chemical form and its rate of application.

The method of application can significantly influence accessibility of nutrients to plants. For example, banding, or applying fertilizer in strips along crop rows, increases nutrient accessibility to roots. Broadcasting or applying fertilizer uniformly over an entire soil surface can place some fertilizer completely outside the root zone of certain crops and thus require a proportionately larger application to assure growth, meaning that there is more available for loss. The form in which fertilizer is applied is another important factor influencing plant uptake and nutrient loss. Soluble nitrogen usually oxidises to nitrite within a few days of application, its chemical form upon application makes little difference to its chances of groundwater transport. However, volatile forms of nitrogen, such as anhydrous ammonia, may be lost to the atmosphere before conversion to nitrate if improperly injected. Urea nitrogen may also be volatilized if improperly applied.

The amount of nitrogen leached from fertilizer is proportional to the total amount of soluble nitrogen in the soil at the time of irrigation.

Residual fertilizer is unavoidable after harvest, however, residual nutrients can be partially used up by multi-cropping, when a new planting is organised to immediately follow harvest. Multi-cropping combined with multiple applications or slow-release nutrients offer the best chance to utilise valuable nutrients.

Nitrogen applied after the target crop's active nitrogen uptake period is unlikely to be used efficiently by the crop. Significant portions of such late-applied nitrogen will be lost to leaching, and lower yields will result due to limited nitrogen uptake.

The crop nutrient needs and the soil nutrient availability should be known in order to evaluate the effectiveness of various fertilization practices. This should be done with a programme of soil testing including soil sampling, sample analysis and adherence to recommended application rates for specific crops.

Irrigation water should be tested for nitrogen content and the nitrogen fertilizer rates adjusted accordingly. Fertilizer nitrogen rates are based on what the crop needs and the appropriate amounts of nitrogen credits from other sources such as soil organic matter, previous legume crops, manures and possible residual nitrogen from the previous year (Schmitt, 1994). It should be noted that relatively small doses of nitrogen in irrigation water can add up to a significant cumulative amount.

Also on irrigated soils, the nitrogen should be applied as close as is practically possible to the time when the crop takes up nitrogen. Split applications are more likely to place the nitrogen in the soil when the crop needs it.

Irrigation scheduled to meet crop water needs in terms of timing and quantity will help maximise crop nitrogen uptake and minimise leaching losses (Hera, 1981). This will also help decrease nitrate leaching under vegetable crops.

A nitrification inhibitor can be included as part of a recommended nitrogen management programme on irrigated soils. The nitrogen inhibitor basically delays conversion of ammonium to nitrate by inhibiting the activity of nitro-bacteria. This preserves a greater fraction of the applied nitrogen in the ammonium form and, since this form is a cation that reacts with the cation-exchange properties of soil clays and organic matter, it is not subject to leaching. Inhibitors are most commonly used with anhydrous ammonia and sometimes urea. Nitrogen applied after the target crop's active nitrogen uptake period is unlikely to be used efficiently by the crop. Significant portions of such late applied nitrogen will be lost by leaching, and lower

yields will result due to limited nitrogen uptake (Schmitt, 1994). Hoefl (1984) concluded that nitrification inhibitors should be considered as a nitrogen management tool and that the benefit to be obtained depends on the soil type, time and rate of application, and the temperature and moisture conditions between time of application and time of use by the crop.

## 9.7 Integrated Pest Management (IPM)

Integrated pest management treats a crop as an ecological system. It uses all control tactics (including chemical pesticides) in a compatible manner to reduce inevitable environmental damage to an acceptable economic level.

IPM uses cultural and other non-chemical controls wherever possible, but it also uses, if necessary, limited, specific applications of a chemical pesticide. The integrated approach tolerates some pests (those that damage part of the crop that is not marketable), so long as the damage remains minor (Environment Canada, 1991).

Multiple cropping (growing two or more crops together in one field) is another approach. In fields where crops are rotated regularly, pests, including weeds, insects and pathogens, do not increase as quickly since they cannot adapt themselves to a constantly changing set of environmental conditions. By growing two crops in a single field, the pest in one may be kept down by predators that inhabit the other (Crosson, 1989).

Non-chemical controls for pests include;

- *Cultural control* - crop rotation, companion planting, timing of planting and harvest, resistant varieties, trap crops, sanitation and baiting of pest habitats with food to lure pests away from plants
- *Mechanical control* - Vacuums, barriers
- *Physical control* - heat, cold, light, sound

Integrated protection is based on the use of all farming methods such as rotation cropping, clones, manure, pesticides, sowing dates and soil preparation which tend to lessen the effect of pests and stimulate the action of useful organisms. Pesticides should only be applied when pests are there, i.e. the treatment is curative rather than preventive (Pelereents, 1990).

## 9.8 Nutrient management practices

Losses of nitrogen and other elements to surface water can be reduced by control of soil erosion. Runoff water containing no soil has very little nitrogen in it.

Nitrate leaching to groundwater can be reduced by managing the nitrogen cycle to maximise the fraction of the available nitrogen in the soil that is used by the crop. The best way to minimise leaching of nitrate is to focus on practices that favour its most efficient use (Aldrich, 1984).

### 9.8.1 Optimum Crop Management

Agronomic management for high yields will promote efficient utilisation of the available nitrogen in the soil-plant system. Selection of crop varieties with high yield potential that are well adapted to local conditions, proper timing of planting, harvesting, proper fertilizer use and proper water practices.

### 9.8.2 Assessment of available nitrogen

Integration or assessment of available nitrogen from the soil, irrigation water, and applied organic materials, can help avoid subsequent overapplication of nitrates.

Soil nitrates consist of mineral nitrogen (ammonium plus nitrate) residual from the previous crop, the nitrogen that will be mineralised from the soil organic matter and the residues from the previous crop. The residue from a grain crop such as wheat will contribute little nitrogen and in fact may cause immobilisation and thus be a nitrogen demanding residue. The residues from alfalfa or other legumes, however, will contribute substantial amounts of available nitrogen because of their high nitrogen contents.

Losses of nitrogen by leaching can be reduced (Dekker, 1984) by applying fertilizer to a wet soil surface which had just been irrigated by sprinklers, and then sprinkling again the next day. In this way the fertilizer grains dissolve and nitrogen diffuses into the surface soil, allowing less nitrogen movement along the soil surface towards the vertical cracks during the next sprinkling.

## **9.9 Biocides under furrow irrigation**

Furrow irrigation system design has also been found to significantly affect the amount of biocide leaching in agricultural areas (Ranjha, 1992). Furrow irrigation design and management affect water-storage efficiency and pesticide leaching. Increasing flow rates at the furrow head or decreasing furrow length improves water storage efficiency and in turn reduces biocide leaching and the risk of potential ground-water contamination.

## **9.10 Precision farming**

Precision farming utilises many of the methods already described the main difference is that it doesn't treat a single field as a single homogeneous entity but instead it splits the field up into smaller zones where different treatments are required. In terms of yields and input costs this can have large benefits as field areas receive the amount of resources they need as opposed to average value which may leave some areas over supplied and others under. This would also reduce the use of agrochemicals as they would be more efficiently used. Problems with much of the technology include the need for large amounts of data and expensive equipment also much of the technology has been created in the developed world. The principles though are still valid and could be adapted to intermediate technology making use of farmers own knowledge.

# **10. RECOMMENDATIONS**

This report provides a number of options for managing agrochemicals and avoiding consequent pollution. Of course every particular situation will have its own circumstances and it is not possible to generalise recommendations on how local authorities should organise their own arrangements for managing agrochemical pollution. On the contrary, such authorities should establish for themselves the range of options available and identify which are relevant to them.

Furthermore, the report has given a detailed overview of the various management aspects – monitoring procedures, modelling possibilities, safe limits, types of agrochemicals, toxicity and/or persistence of agrochemicals and has accumulated a wide range of references through which further details can be sought. Its purpose is to act as a reference guide and a resource document for capacity building.

## **10.1 Monitoring**

There is need for more support for monitoring of pollution such as agrochemicals, and for data-processing exercises. Action to better manage such processes is far more likely to be implemented by government authorities if the need is based on collected information that identifies the nature of the pollution and whether it is following a trend. Monitoring of agrochemicals is made difficult by the enormity of making regular measurements over a wide area, which is not feasible with the staff and financial resources available.

Such monitoring can be integrated into a wider environmental impact programme in which water samples are sent for standard analysis at an environmental laboratory, or by using the WQM (Water Quality

Monitoring) Field-kit approach recently developed (Pearce, 1998). Field-kits can be utilised by suitable field staff for monitoring both nutrients and biocides. Nutrient concentrations are relatively easy to measure using portable comparator photometers. Biocides have hitherto been impossible to measure outside of the specialist laboratory because of their very low concentrations, because there are a very large number of chemical pollutants and because of the complexity of making the assessment. Recent field-kit approaches using the ELISA approach (Enzyme-linked Immuno-assay) contain sophisticated analytical processes that are relatively easy to use. However only one or two biocides or other complex reagents, can realistically be monitored in any one programme.

## 10.2 Critical issues

### 10.2.1 Scale of agrochemical usage in Developing Countries

Agrochemical pollution is widely attributed to over application carried out as part of a management strategy to achieve maximum yield, or value, of crops. This has no doubt been true in many parts of the world such as North America and Western Europe, however it is not necessarily a major problem everywhere. In Developing Countries, local farmers more generally grow subsistence crops and are less concerned about maximising profit from cash crops. For this reason, as well as their much reduced ability to purchase expensive inputs, there is a limit to the amount of agrochemicals they utilise. Concentrations are further reduced by the ability of local eco-systems to absorb small excesses, and also by the take-up by farmers of Integrated Pest Management (IPM) techniques.

There is, throughout the world, a self-evident need to set up sustainable agricultural systems. The trend in Developing Countries seems already to be in this direction. It can be enhanced by encouraging wider use of techniques such as IPM, by the development and provision of more carefully targeted biocides, and by encouraging farmers to be accountable about their environment.

### 10.2.2 Training needs of farmers

There is a basic need for provision of education/awareness programmes for farmers that will encourage the trend to the sensible use of agrochemicals. Furthermore, there appears to be considerable scope for misuse and accidents through dumping unwanted agrochemicals into waterways or through washing out agrochemical containers and equipment. Also there is a need for farmers to be better equipped with protective measures – since this is the principal mechanism by which agrochemicals cause ill-health.

### 10.2.3 Training needs for local departments

There is a need for local officials to be suitably equipped, through education and the allocation of sufficient resources to deal with problems concerning the manufacture and marketing of agrochemicals. Although the scope for dumping old, unsuitable agrochemicals for resale at low-cost is declining, thanks to greater self-regulation, there is scope for local manufacturers to make up old formulations. This needs to be firmly discouraged by appropriate and enforceable legislation.

There is also a need to ensure that the agrochemicals manufactured locally are pure. If they contain significant impurities they will not be so effective and farmers will need to increase applications in order to achieve their target. However the impure components, though not lethal against the targeted pest, may have profound impacts downstream. An example is the manufacture of Lindane, which comprises the  $\gamma$ -isomer form of HCH. The  $\alpha$ ,  $\beta$  and  $\delta$  isomers are not acceptable. The problem needs to be dealt with by better quality assurance in factories, by better monitoring of agrochemical production and by better monitoring of local arrangements for marketing and distributing agrochemicals.

## 10.3 Enabling framework to control agrochemical pollution

In order to achieve effective management of the use of agrochemicals in Developing Countries there is a need to promote and strengthen the following framework.

### Technical training

Training is urgently needed (as described in the previous sections) from a range of levels from safe use by farmers up to the techniques used by local departments to manage agrochemical strategies in their areas.

### Best management practices

BMPs should be incorporated into project designs. They should promote sustainable and safe practices.

### Legislation

If not already in place, the establishment of an effective and enforceable legislation is a crucial step in controlling agrochemical pollution. This needs to define standards for the types of agrochemicals used, the safety measures required, and the concentrations in receiving waters at which agrochemical pollution is not acceptable.

### Monitoring

Local authorities need to ensure that their environmental monitoring programmes are capable of detecting agrochemicals, if it is suspected that they might cause pollution/health problems. Such monitoring should include regular surveillance so that particular problems, such as the dumping of agrochemicals into a drain, can be dealt with. It should also enable seasonal trends to be detected.

### Compliance

The benefits of passing legislation and setting up monitoring programmes will be negated if the local authorities do not receive support from the relevant enforcement agencies. It is important to complete the enabling framework by providing sufficient investment, training and encouragement.

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# *Tables*

**Table 1 Equivalences of nitrogen-based nutrients**

<b>Nitrogen equivalent concentration</b>	<b>Intermediate equivalent concentration</b>	<b>Nitrate equivalent concentration</b>
10mg/l nitrate nitrogen	-	45.6mg/l nitrate
10mg/l ammonium nitrogen	12.9 mg/l NH <sub>4</sub>	45.6mg/l nitrate
10mg/l ammonium nitrate nitrogen	28.6 mg/l NH <sub>4</sub> NO <sub>3</sub>	45.6mg/l nitrate
10mg/l ammonia nitrogen	12.1 mg/l NH <sub>3</sub>	45.6mg/l nitrate
10mg/l urea nitrogen	21.4 mg/l urea	45.6mg/l nitrate

**Table 2 Persistence of selected pesticides in soils**

<i>Low persistence (half-life less than 30 days)</i>	Methyl parathion Sulphur 2, 4-D
<i>Moderate persistence (half-life 30-100 days)</i>	Maneb Mancozeb Carbaryl Diazinon Dinoseb Glyphosphate Simazine
<i>Persistent (half-life 100 days - 1 year)</i>	Benomyl Endosulfan Diuron
<i>Very persistent (half life more than one year)</i>	Paraquat Dieldrin DDT

(Source: Warner,1985 reproduced from Conway 1991)

**Table 3 Maximum Admissible Concentrations (MACs) of nitrates**

	<b>Present MAC</b>	<b>Planned MAC</b>	<b>Guideline</b>
EC	50 mg/l nitrate	25 mg/l nitrate	
WHO	45 mg/l nitrate		25 mg/l nitrate
USEPA	10 mg/l N-nitrate = (45 mg/l nitrate)		
USDA	20 mg/l nitrate		
Canada			1 mg/l nitrate



**Table 4 Maximum admissible concentrations (MACs) for biocides in drinking water (µg/l)**

	<b>World Health Organisation (WHO)</b>	<b>European Communities (EU)</b>	<b>Dept of the Environment (UK)</b>	<b>Environmental Protection Agency (USA)</b>
<b>Herbicides</b>				
Obtrusion	2	0.1	30	150
Simazine	17	0.1	30	1500
Alachlor	0.3	0.1		
Propanil	170	0.1		
MCPA	0.5	0.1	10	
Trifluralin	170	0.1		
2, 4-D	100	0.1	100	100
Paraquat	0.3	0.1	0.3	60
Molinate	7	0.1		
Isoproturon	0.4	0.1		
<b>Insecticides</b>				
Aldicarb		0.1	7	10-30
Dimethoate	7	0.1	7	
Endrin		0.1		0.2
γHCH (Lindane)		0.1.		4

Source: Lawrence (1987) and Holden (1986) in Conway (op cit 1991)

**Table 5 USEPA Health Advisories for pesticides in drinking water**

<b>Pesticide</b>	<b>Lifetime health advisory <math>\mu\text{g l}^{-1}</math></b>
Acifluorfen	1
Alachlor	0.4
Aldicarb and aldicarb sulphoxide	10
Aldicarb sulfone	40
Ametryn	60
Ammonium sulphamate	1500
Atrazine	3
Bentazon	20
Bromacil	90
Butylate	700
Carbaryl	700
Carbofuran	40
Carboxin	700
Chloramben	100
Chlordane	0.03
Chlorthalonil	2
Cyanazine	10
Dalapon	200
Diazinon	0.06
DBCP	0.03
1,2-Dichloropropane	0.6
<b>Pesticide</b>	<b>Lifetime health advisory <math>\mu\text{g l}^{-1}</math></b>
1,3-Dichloropropane	0.2
DCPA	3500
Dicamba	200
2,4-Dichlorophenoxyacetic acid (2,4-D)	70
Dieldrin	0.00
Dimethrin	2100
Dinoseb	7
Diphenamid	200
Disulfoton	0.3
Diuron	10
EDB	0.00
Endothal	140
Endrin	0.3
ETU	0.2
Fenamiphos	2
Fluometuron	90
Fonofos	14
Glyphosate	700
Heptachlor/heptachlor epoxide	0.00
Hexachlorobenzene	0.02
Hexazinone	200
Lindane	2

**Table 5 (continued)**

Maleic hydrazide	3500
MCPA	3.6
Methomyl	200
Methoxychlor	400
Methyl parathion	2
Metolachlor	100
Metribuzin	200
Oxamyl	200
Paraquat	3
Pentachlorophenol	200
Picloram	500
Prometon	100
Pronamide	50
Propachlor	90
Propazine	10
Propham	100
Propoxur (BAygon)	3
Siamazine	4
Tebuthiuron	500
Terbacil	90
Terbufos	1
Toxaphene	0.03
2,4,5-T	70
2,4,5-Trichlorophenoxypropionic acid	50
Trifluralin	2

Issued USEPA (1990).

**Table 6 Computer models for predicting the impacts of agrochemicals**

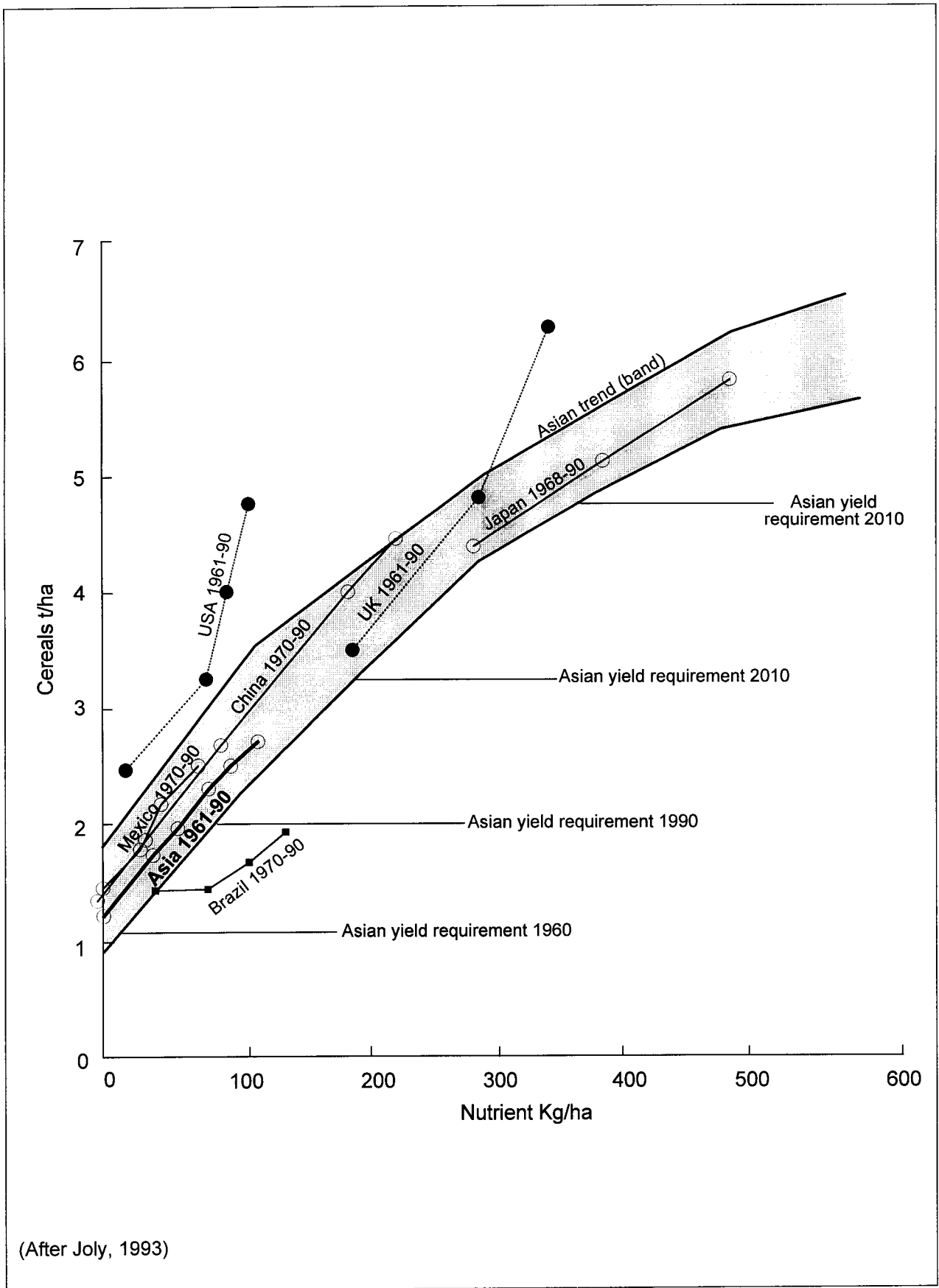
	<b>Purpose</b>	<b>Further details</b>	<b>Comments</b>
ANIMO	Nitrate leaching model	Berghuijs, 1985, NL	Use with hydrological model
ANSWES	Field scale evaluation of nutrients, pesticides, hydrology and soil erosion		Areal Non-point Source Watershed Environment Response Simulation
EXAMS II	Environmental model of stream system used to predict pesticide concentrations in surface waters	Burns, 1985, USA	
CHEMFLO			
CREAMS	Describes pesticide movement processes and run-off from fields (but not leaching to groundwater)	Beasley, 1989, USA	Chemicals Runoff And Erosion from Agricultural Management Systems
DAISY	Nitrate leaching analysis and prediction	Hansen, 1991, Denmark	Simulates denitrification capacity. Has own hydrological model.
EPIC	Nitrate leaching model, includes hydrology and soil erosion	Williams, 1984	Erosion Productivity Impact Calculator uses GLEAMS algorithms to assess erosion effects.
GLEAMS	Widely used model for chemical run-off and leaching evaluations	Leonard, 1987, USA	Single program system for Groundwater Leaching Effects of Agricultural Management Systems but can only simulate root zone, not saturated zone.
HERBASYS	Expert system for giving herbicide advice	Gottesburen, 1991, Germany	HERBicide Advisory SYStem supports agricultural extension services
LEACHM-P	Predicts concentrations for pesticides but does not consider runoff	Waganet, 1987, USA	Leaching Estimation And Chemistry Model - Pesticides, estimates flow, pesticide transport and degradation.
HSPF	Suite of models that integrate field data into watersheds and streams, but not extensively used for pesticide run-off.	Johansen, 1984, USA	Hydrologic Simulation Program - FORTRAN
NFLOOD	Simulates Nitrogen dynamics in saturated soils	Jayaweera, 1990, USA	
NLEAP	Screening tool for nitrate leaching	Shaffer, 1991, USA	Nitrate Leaching and Economic Analysis Package
PESTAN			
PRZM	Models pesticide movement and degradation in groundwater	Dean, 1989, USA	Pesticide Root Zone Model, - has been updated to PRZM2 with a hydrological option for slowly permeable soils and irrigation. RUSTIC links PRZM to vadose zone processes. Can not handle more than one compound, nor volatiles.
RITZ			
RZWQM	Modular, physically based model of non-point pollution	Decoursey, 1990, USA	Root Zone Water Quality Model (includes OMNI for Organic Matter Nitrogen)
SOIL-N	Nitrate leaching assessment	Johnsson, 1987	Used with hydrological model
SUTRA			
SWATNIT	Steady-state model for nitrate leaching at a regional scale	Vereecken, 1990	Has own hydrological model
SWRRB	Models pesticide runoff processes like CREAMS but covers multiple watersheds and edge-of-field calculations	Arnold, 1990, USA	Simulator for Water Resources in Rural Basins
VS2/T			
VLEACH			

NB This list is intended to demonstrate the wide range of situations that are being modelled and the wide range of models developed. It is by no means exhaustive and the inclusion of the models should not be taken as an endorsement.

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# *Figures*



**Figure 1 Fertilizer use throughout the world**

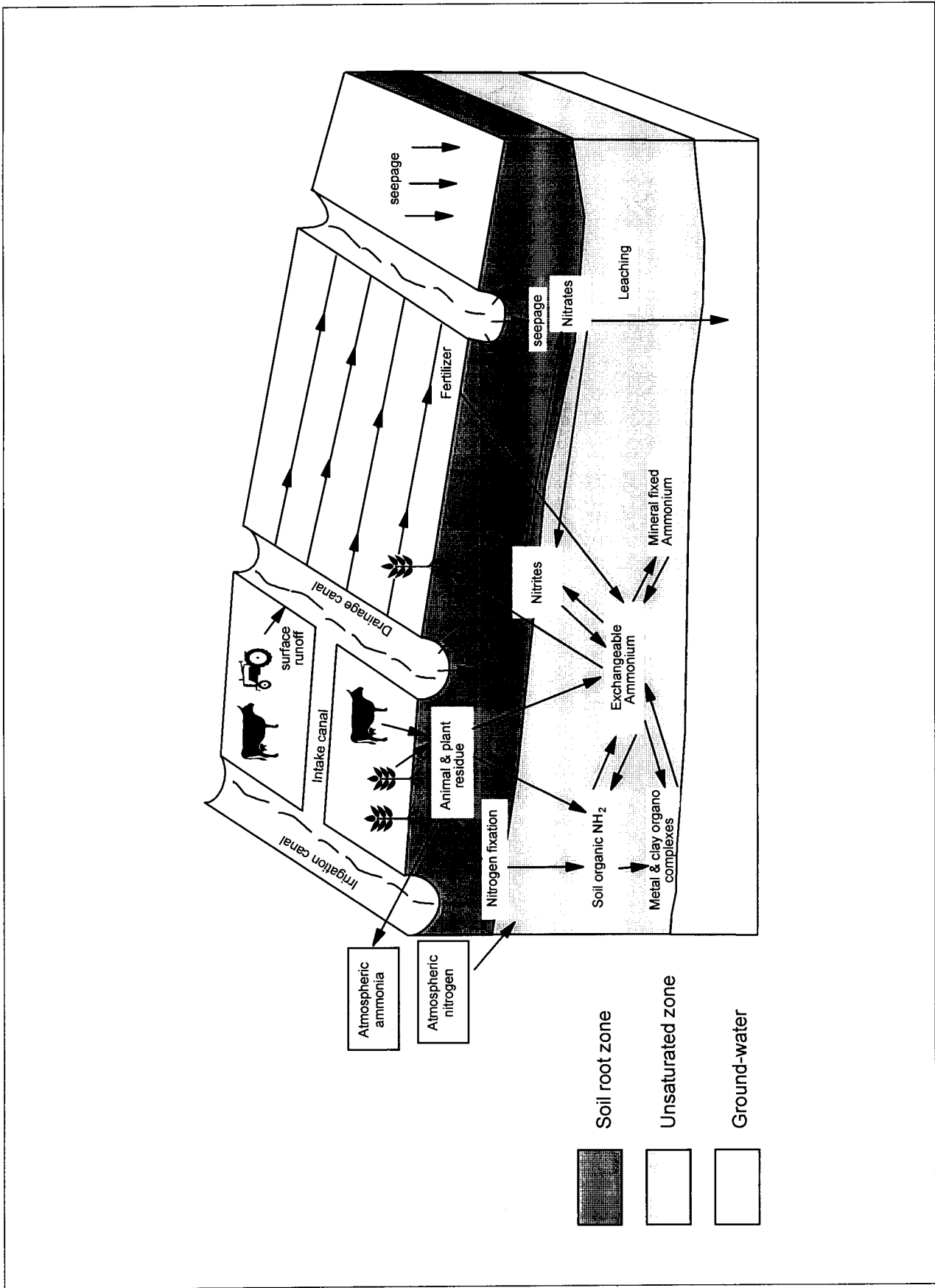


Figure 2 Denitrification



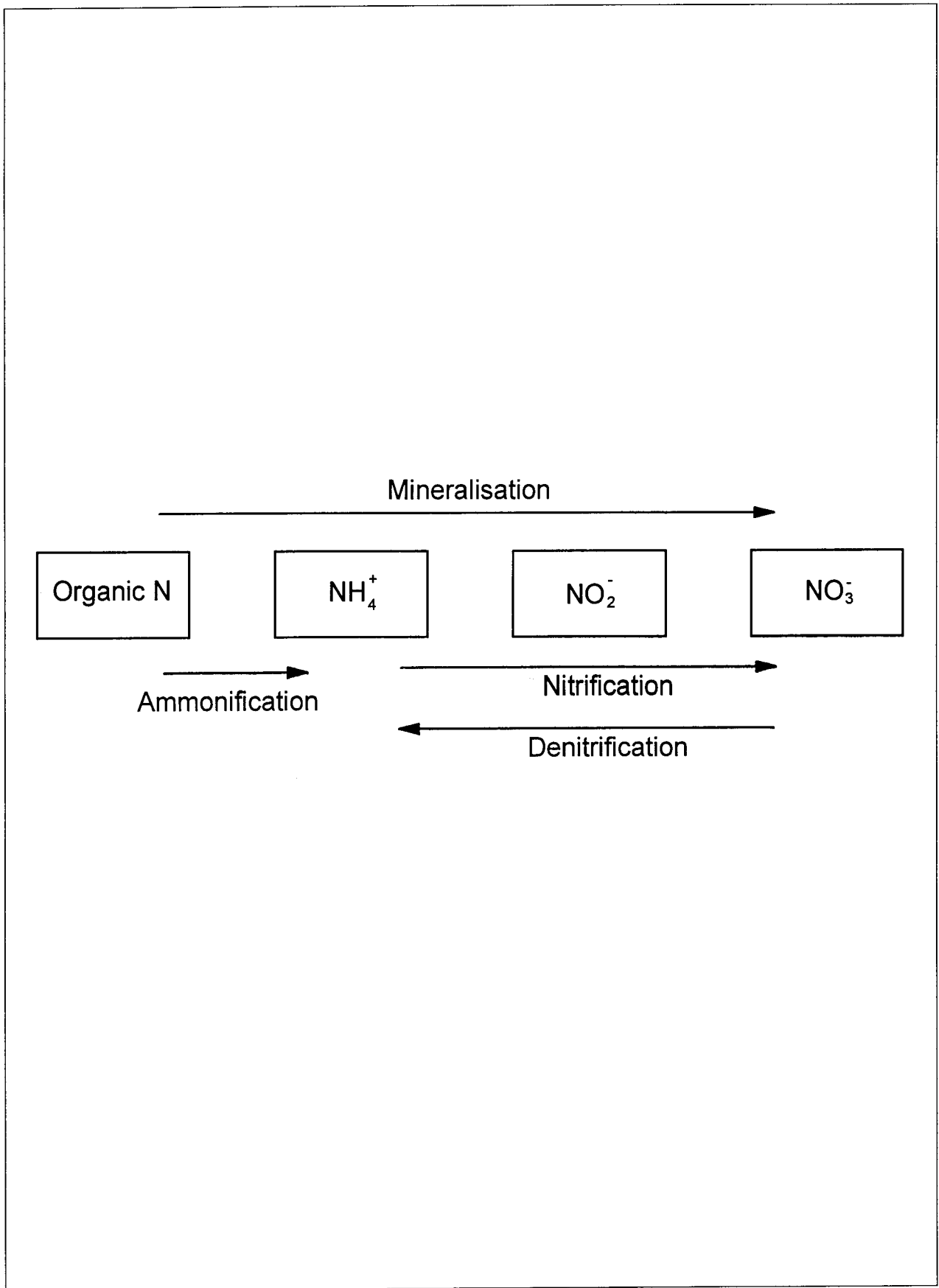
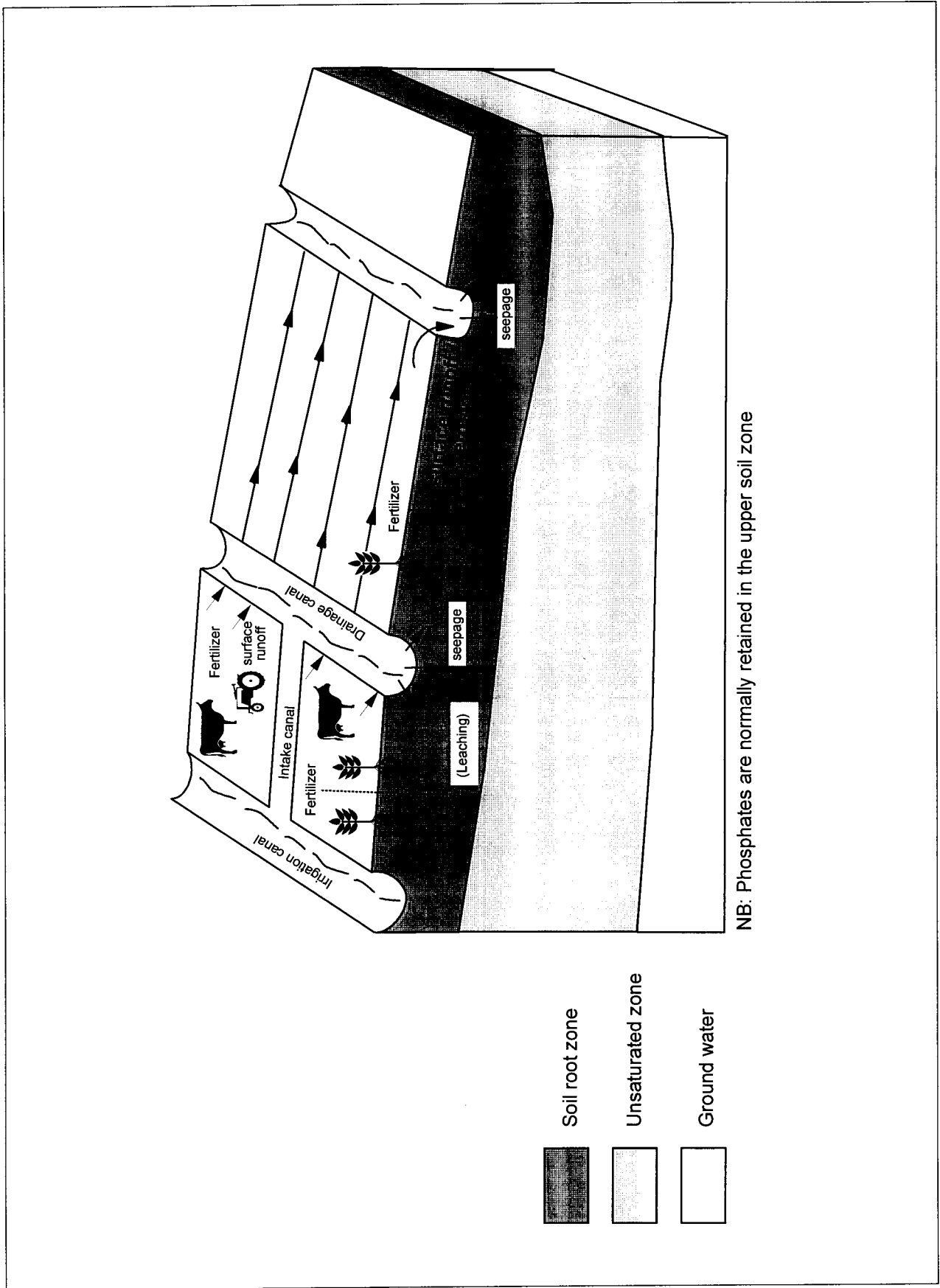
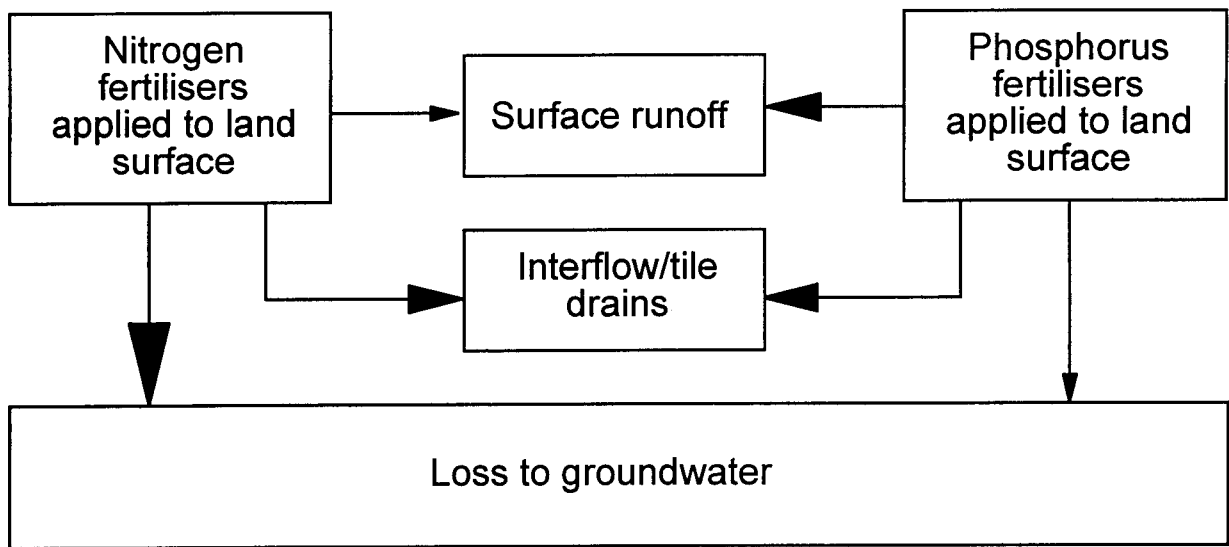


Figure 3 Mineralisation of nitrogen



**Figure 4 Phosphorus cycle in an irrigation scheme**



(Arrow size is proportional to significance of loss)  
After Ongley, 1996

Figure 5 Nutrient loss processes

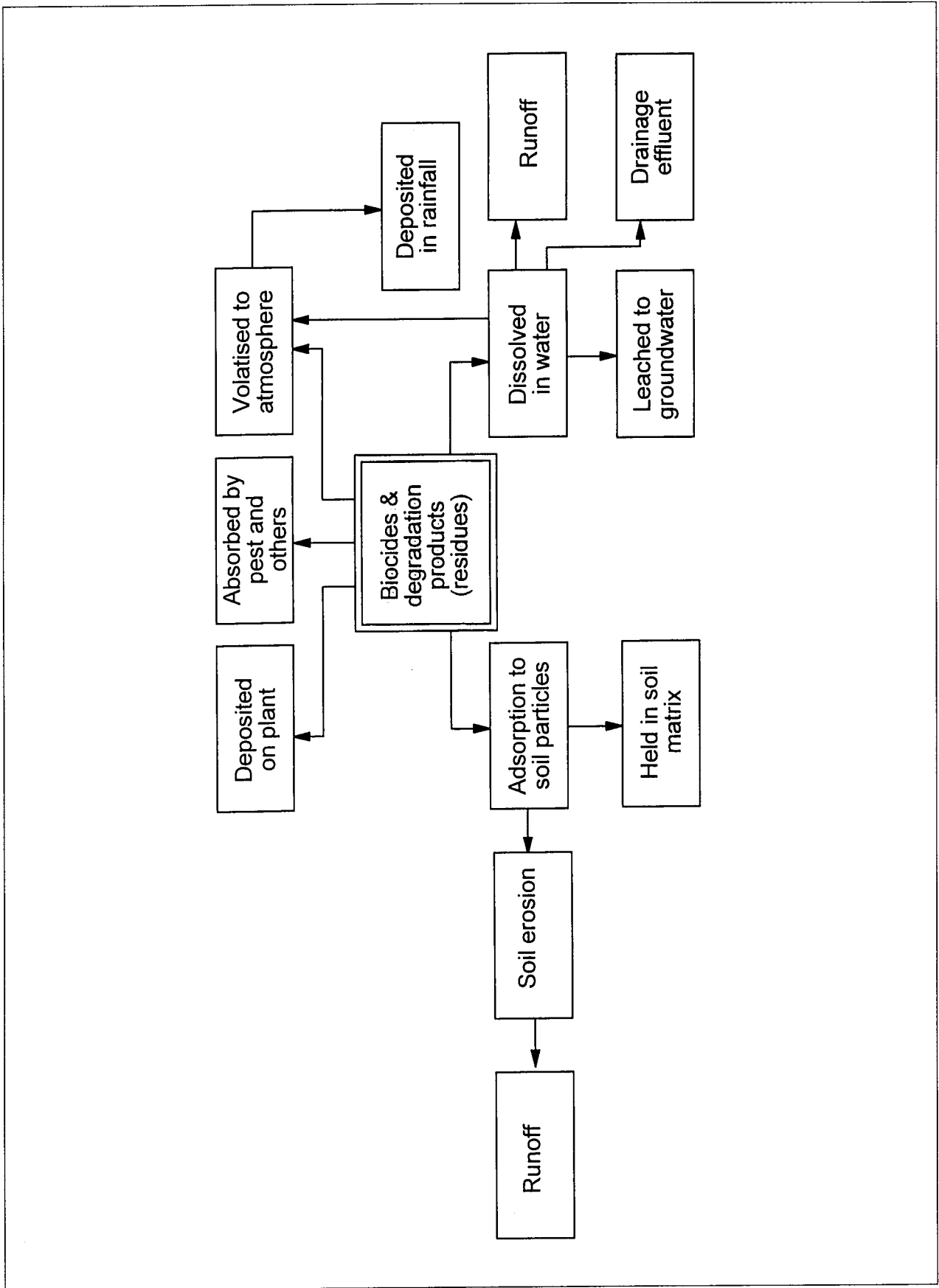
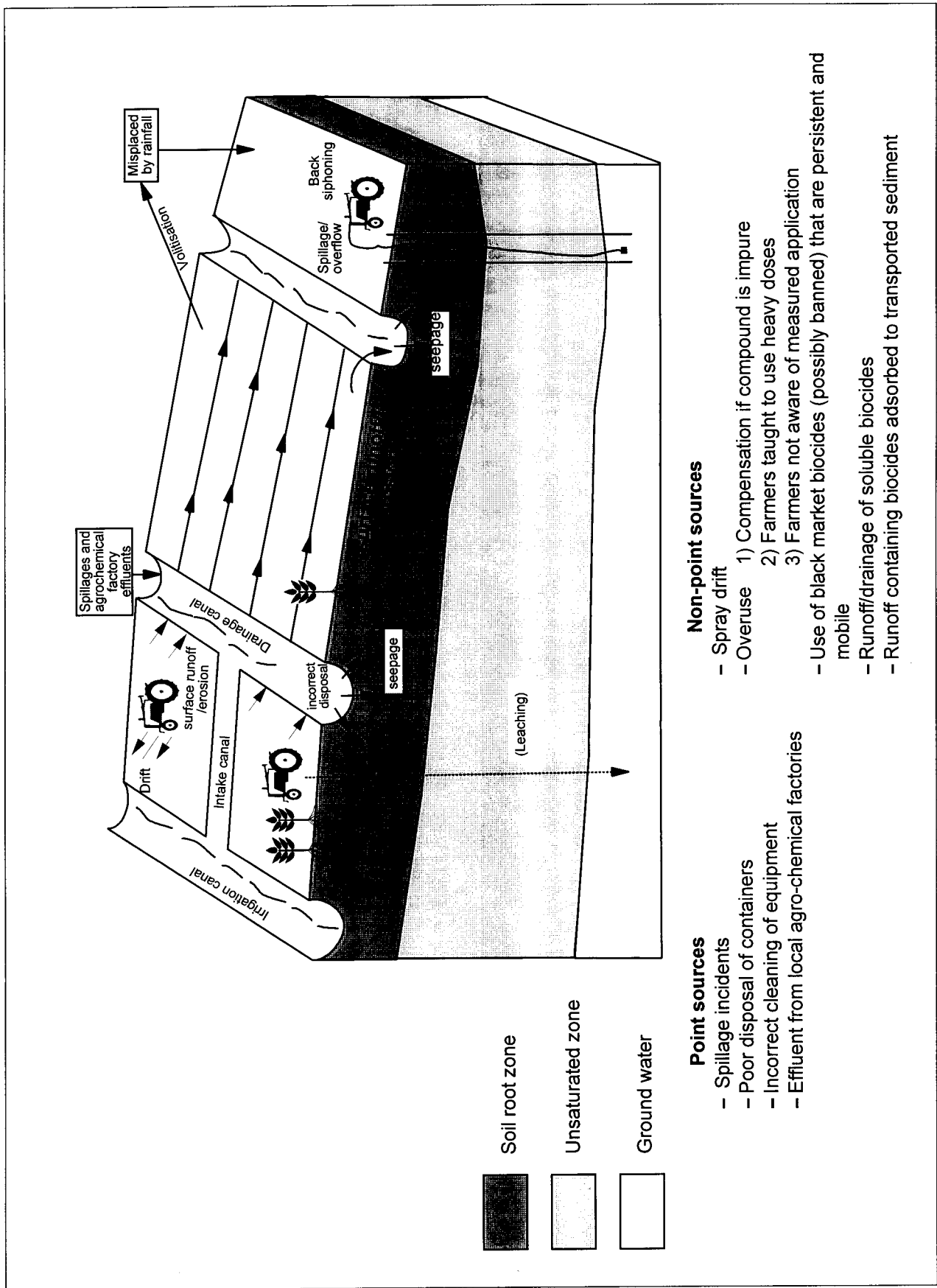
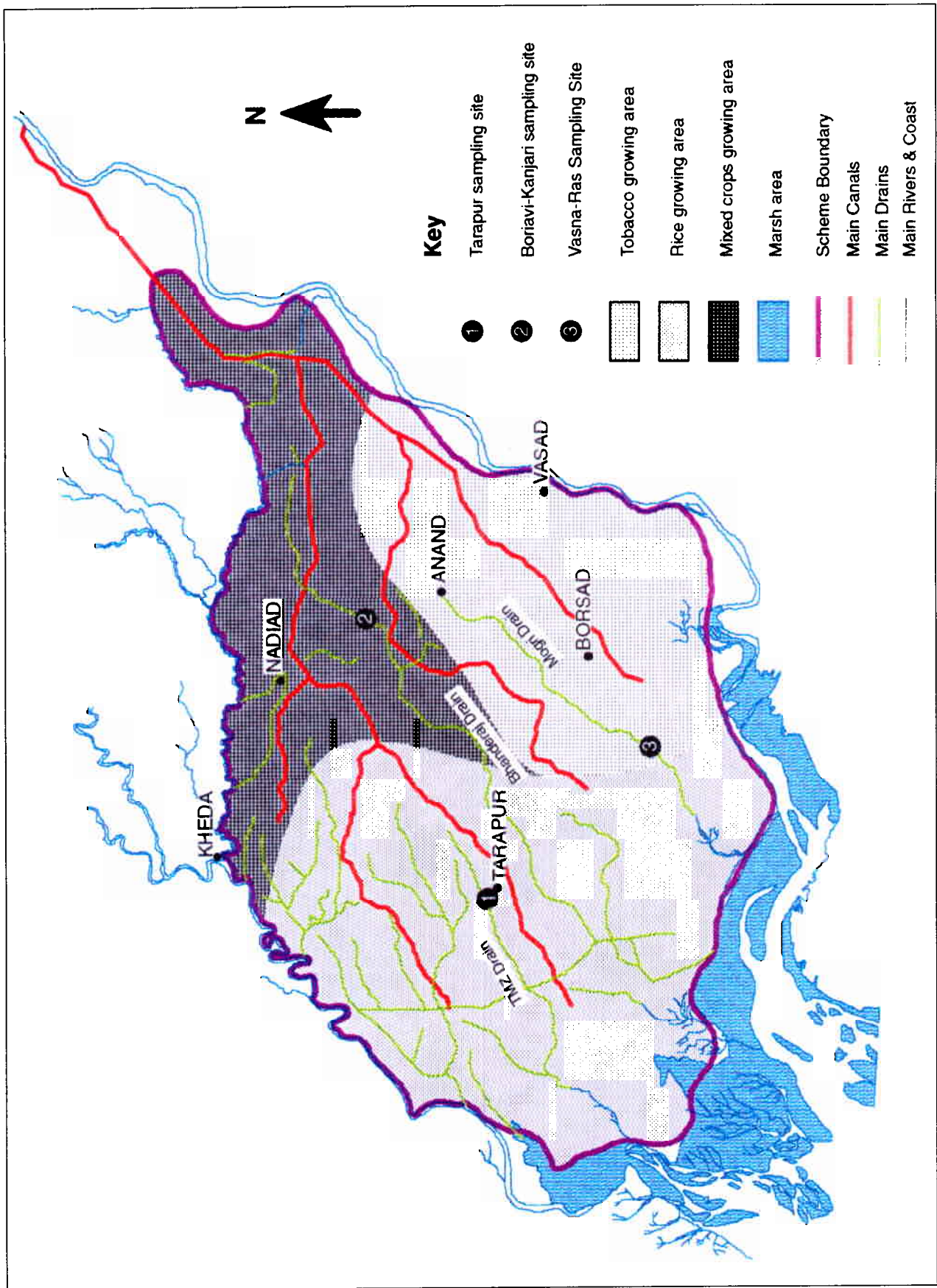


Figure 6 Biocide loss processes



**Figure 7 Biocide movement in an Irrigation scheme**



**Figure 8** Location of sampling sites within the main cropping areas of an irrigation scheme, Northern India

# *Appendices*

# ***Appendix 1***

Uses and characteristics of major biocides





## Appendix 1 Use and characteristics of major biocides

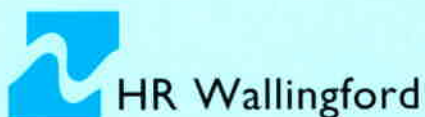
Pesticide	Use	Persistence Half Life	Drinking Water Level ( $\mu$ g/l)	Dirty Dozen (DD) / Persistent Organic Pollutants (POPs)
Acifluoren	Herbicide for use in soybeans, groundnuts and rice etc			
Alachlor	Herbicide for use in maize, soybeans and groundnuts		2 (USEPA) 20 (WHO)	
Aldicarb	Pesticide for use in cotton, sugar beet, potatoes etc. Controls nematodes in soil and insects/mites on crops		10 (USPEA) (WHO)	
Aldicarb sulfone			40 (USEPA)	
Aldicarb sulfoxide			10 (USEPA)	
Aldrin	Chlorinated Insecticide for soil insects		0.03 (WHO)	DD POP
Ametryn	Herbicide for use in pineapple, sugarcane, bananas, maize, and potatoes			
Atraton	Experimental herbicide			
Atrazine	Selective herbicide for use in maize, sugarcane, pineapple, and citrus fruits	(months)	3 (USEPA) 2 (WHO)	POP
Atrazine deethylated				
Barban	Herbicide for use in wheat, lentils, peas, sugarbeet, barley and clover			
Baygon	Insecticide for cockroaches, flies, mosquitos and turf insects			
Benomyl	Fungicide for field crops	100-365d		
Bentazone	Herbicide for use in soybeans, rice, maize, groundnuts, beans, peas, and mint. Photodegrades, but is mobile		30 (WHO)	
Bromacil	Herbicide for use in citrus and pineapple			
Butachlor	Herbicide for use in rice and other crops			
Butylate	Herbicide for use in grassy weeds	30-100d		
Carbaryl	Insecticide for use in forests and rangeland			
Carbofuran	Insecticide to control mites and nematodes etc. It is sufficiently mobile and persistent to be mobile		40 (USEPA)	
Carbofuran, 3-hydroxy			5 (WHO)	
Carbofuran, phenol				
Carbofuran, phenol, 3-keto				
Carboxin	Fungicide for use in barley, oats, wheat and seedlings			
Chloramben	Herbicide for use in soybeans, groundnuts, sunflowers and maize			
Chlordane	Insecticide to control termites		2 (USEPA) 0.2 (WHO)	DD POP
Chlorobenzilate	Acaricide to control mites			
Chloroneb	Fungicide to control seeding diseases			
Chloropicrin	Insecticide for stored grain and nemacide for soil			POP
Chlorothalonil	Fungicide for use in beans, carrots, maize etc			
Chlorpropham	Herbicide for use in alfalfa and beans			
Cyanazine	Herbicide for use in fallow cropland			
Cycloate	Herbicide to control weeds and grasses			

2,4-D (Dichloropheno oxyacetic acid)	Herbicide for use in wheat, maize and barley	<30d	70 (USEPA) 30 (WHO)	
Dalapon	Herbicide to control annual grasses		200 (USEPA)	
2,4-DB	Herbicide for use in alfalfa, soybeans and groundnuts	(days)	90 (WHO)	
DCPA  DCPA acid metabolites	Herbicide for use in fruits & vegetables			
4,4-DDD  4,4-DDE  4,4-DDT	Insecticide to control mosquitoes and spiders. Very stable and persistent.	+365d	2 (WHO)	DD POP  DD POP  DD POP
Diazinon	Soil insecticide for worms and maggots in fruit & vegetables	30-100d		
Dibromochloro propane (DBCP)	Soil fumigant to control nematodes		0.2 (USEPA) 1 (WHO)	
Dicamba	Herbicide for use in maize, sorghum etc			
Dicamba, 5- hydroxy	Herbicide for use in asparagus, cereals, maize etc			
3,5- Dichlorobenzoic acid	Herbicide to control perennial grasses			
1,2 Dichloropropane	Soil fumigant		5 (USEPA) 20 (WHO)	
1,3 Dichloropropene	Nematocide for use in soil		20. (WHO)	
Dichlorprop	Herbicide for use in cereals and pastures		100 (WHO)	
Dichlorvos	Insecticide for use in fruit and vegetables			
Dieldrin	Insecticide for soil insects such as locusts	+365d		DD POP
Dinoseb	Herbicide for use in potato vines	30-100d	7 (USEPA)	
Diphenamid	Herbicide for use in groundnuts, tobacco and alfalfa			
Disulfoton  Disulfoton sulfone  Disulfoton sulfoxide	Insecticide for use in seeds			
Diuron	Herbicide for use in wheat, barley and bananas	100-365d		
Endosulfan I  Endosulphan II  Endosulphan sulfate	Insecticide for use in cereals, coffee, cotton, fruit, potatoes etc	100-365d		
Endrin  Endrin aldehyde	Insecticide for use in cotton & small grains		2 (USEPA)	DD POP
EPTC	Herbicide for use in beans, potatoes and maize			
Ethoprop	Nematocide/Insecticide for use in bananas.			
Ethylene dibromide (EDB)	Insecticide for use on soil. Degrades but is persistent when dissolved in water.		0.05 (USEPA)	POP
Ethylene dichloride (EDC)	Insecticide for product stores			POP
Ethylene thiourea (ETU)	Fungicide for use in flowers, potatoes, tomatoes etc			
Etridiazole	Soil fungicide for use in beans, maize, cotton, sorghum			

Fenamiphos Fenamiphos sulfone Fenamiphos sulfoxide	Insecticide for use in cotton, soybeans, vegetables & fruit			
Fenarimol	Fungicide for mildew on fruit and flowers			
Fluometuron	Herbicide to control annual grasses			
Fluroacetic acid	Rodenticide and systemic insecticide			POP
Fluridone	Herbicide to control for annual grasses in cotton			
Glyphosate (4)	Nonselective broad spectrum herbicide for use in cereals and beans etc	30-100d	700	
$\alpha$ -HCH $\beta$ -HCH $\gamma$ -HCH $\delta$ -HCH	Contaminants of the $\gamma$ form Contaminants of the $\gamma$ form Insecticides for use in rice and wood Lindane – Persistent with low affinity for water and low mobility for soil Contaminants of the $\gamma$ form		0.2 (USEPA) 2 (WHO)	POP
Heptachlor (2) Heptachlor epoxide	Broad spectrum Insecticide for use in maize particularly mites Persistent, particularly as epoxide. Migrates slowly.		0.4 (USEPA) 0.3 (WHO)	DD POP
Hexachlorobenzene (HCB)	Fungicide for use in wheat		1 (WHO)	DD POP
Hexazinone	Herbicide for use in sugarcane, pineapple etc			
Linuron	Herbicide for use in maize, carrots, potatoes etc			
Maneb	Fungicide for use in field crops	30-100d		
Mencozeb	Fungicide for use in potatoes, tomatoes, apples etc	30-100d		
Merphos	Defoliant for use in cotton			
Methiocarb	Insecticide for use in cherries			
Methomyl	Broad spectrum insecticide for use in agricultural crops			
Methoxychlor	Insecticide for use in fruit and trees. Poorly soluble and highly immobile.		400 (USEPA) 20 (WHO)	
Methyl paraoxon	Insecticide for a wide variety of insects			
Methyl parathion	Insecticide	<30d		
Metolachlor	Selective, pre-emergent. Herbicide for use in sunflowers and maize		10 (WHO)	
Metribuzin Metribuzin DA Metribuzin DADK Metribuzin DK	Herbicide for use in soybeans, wheat, barley & lentils etc			
Mevinphos	Insecticide to control mites, beetles etc on fruit & vegetables			
MDK 264	Synergist for pyrethrin, allethrin & rotenone			
Mirex (2)	Insecticide			DD POP
Molinate	Herbicide for use in rice		6 (WHO)	
Napropamide	Herbicide to control annual grasses			
Neburon	Herbicide to control weeds & grasses			
Nitrofen	Herbicide for use in cereals			POP
4-Nitrophenol	Fungicide for use in pears			
Norflurazon	Herbicide for use in cotton, nuts and cranberries etc			
Oxamyl	Insecticide for use in crops and fruits			

Paraquat	Systematic herbicide for grand clearance	+365d		POP
Pentachlorophenol (PCP)	Fungicide /insecticide for use on timber		200 9 (WHO)	
Pebulate	Herbicide for use in sugarbeet, tobacco and tomatoes			
Permethrin	Pyrethroid Insecticide for use in cotton and in mosquito control. High affinity for soil, low affinity for water.		20 (WHO)	
Picloram	Herbicide for use in woody plants & pastures		500 (USEPA)	
Polychloroterpenes	Insecticide & acaricide			POP
Prometon	Herbicide to control perennials & grasses in non-crop areas			
Prometryn	Herbicide for use in cotton, peas, carrots and vegetables			
Pronamide	Herbicide for use in lettuce, legumes etc			
Propachlor	Herbicide to control grasses			
Propanil	Herbicide for use in rice – water affinity		20 (WHO)	
Propazine	Herbicide for use in sorghum			
Ropham	Herbicide for use in alfalfa, lettuce, spinach, sugarbeet, lentils etc			
Quintozene	Fungicide for use in seed and soil			POP
Simazine	Herbicide for use in crops and fruit. Fairly persistent and mobile	30-100d	1 (USEPA) 2 (WHO)	
Simetryn	Herbicide for use in rice			
Stirofos	Insecticide for use in maize, cotton, vines and fruit			
Sulphur	Acaricide/fungicide	<30d		
Swep	Herbicide for use in rice & maize etc			
2,4,5-T	Herbicide to control woody plants in industrial areas		9 (WHO)	
Tebuthiuron	Herbicide for use in non-crop and rangeland			
Terbacil	Herbicide for use in sugarcane, alfalfa, apples, peaches etc			
Terbufos	Insecticide for use in maize, vegetables and sorghum			
Terbutryn	Herbicide for use in winter wheat and barley			
Toxaphene (2)	Insecticide/Acaricide			DD POP
2,4,5-TP Trichlorophenol	Herbicide for use in rangeland, sugarcane and rice		50 (USEPA)	
Triademefon	Fungicide for use in vegetables, cereals, coffee and fruit			
Tricyclazole	Fungicide for use in seeded rice			
Trifluralin	Herbicide for use in soy beans, cotton and vegetables		20 (USEPA)	
Vernolate	Herbicide to control broadleaf and grassy weeds			

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