Identification and Quantification of Groundwater Nitrate Pollution from Non-agricultural Sources

Literature review

British Geological Survey

R&D Technical Report P33

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Literature Review

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Statement of use
This report summarises the available literature on groundwater pollution from non-agricultural nitrate. The information within this document is for use by EA staff and other involved with the review of Nitrate Vulnerable Zones, where the catchment is not wholly arable land.

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EXECUTIVE SUMMARY

Nitrate has been identified as, and remains, a major water quality issue in the UK, and it originates as a diffuse pollutant in all of the major aquifers and many of the minor aquifers of England and Wales. Considerable scientific effort has been devoted to understanding and quantifying the behaviour of nitrogen inputs from normal agricultural practices, and their transport to groundwater. However, there are other potential sources of nitrate which can affect groundwater. Some of these activities are completely non-agricultural, whilst others are non-arable agricultural, and most are poorly characterised and quantified at present. As a result the Environment Agency (EA) could potentially be vulnerable to criticism from farmers, landowners and their representatives for taking a perceived partial and non-scientific approach to the implementation of new European legislation. Under the Nitrate Directive, review of existing Nitrate Vulnerable Zones (NVZs) and new candidate NVZs will be carried out every four years. The first review is due to be completed by the end of 1997, and the EA will be providing technical support to the UK government. Scientifically robust yet relatively simple methods need to be used for establishing a balanced perspective of the contributions from non-agricultural, non-arable agricultural and arable agricultural activities.

As the first phase of this process, a focused literature review of studies of nitrogen loading and groundwater pollution from non-agricultural sources of nitrogen has been produced. A number of potential sources have been identified:

- urban or suburban areas, the recharge from which may include leakage from sewers and septic tank effluents
- infiltration of river-borne effluent from sewage treatment works in losing reaches of rivers
- application of sewage and other sludges to land as a disposal practice
- atmospheric deposition of nitrogen
- use of urea-based de-icing compounds at airfields
- recreational use of fertilizers in parks, golf courses and playing fields
- disposal of wastes from intensive livestock farming
- landfill leachates
- highway drainage

The published scientific literature was accessed through various library retrieval systems. Unpublished material or work put out by research institutes or funding agencies was obtained by a direct approach to the relevant organizations. An indication of the relative importance of the sources is provided by the amount of published material and current research devoted to each source. Thus, atmospheric deposition has been recognised as important, has been extensively researched in the UK, and is now relatively well characterised. With tighter controls on atmospheric pollution and vehicle emissions, this may become a more restricted source in the future. Leaking sewers and sludge application to land are important and likely to become more so, and this is reflected in the recent and current research interest.

The leaching losses and the observed nitrate concentrations in the infiltrating recharge and underlying groundwater are required for evaluating the importance of each of the non-agricultural sources. It is clear that such data are lacking in many areas, and the most significant areas of remaining uncertainty for each of the non-agricultural nitrate sources are summarised. Information on the scope and extent of each source would enable them to be ranked in importance nationally, and for their impact on the overall nitrogen budget for NVZs or potential NVZs to be assessed. At a catchment scale, assessment of the impact or contribution from several possible sources would require knowledge of the area affected and the hydraulic loading or surcharge associated with each potential source.

Leaking sewers in urban and suburban areas and sludge application to land above aquifers appear to be the most important non-agricultural sources. Both are widespread but difficult to quantify. Land application of sewage sludge should be prevented in Source Protection Zone I areas of supply catchments and controlled in Zones II and III within the Agency's Policy and Practice for the Protection of Groundwater, and in any case following of the Code of Good Agricultural Practice should prevent excessive applications to agricultural land. Neither of these two potential sources of groundwater nitrate can be adequately characterised without the assistance of the water utilities.

Septic tank systems have limited usage in England and Wales and are unlikely to be a major source of groundwater nitrate. In some cases, individual septic tanks may be providing a contribution to groundwater nitrate, but this is only likely to affect a very small proportion of the overall catchment recharge.

Where there is scope for exchange of water and solutes between surface water and groundwater, then it is clear that the quality of the latter could be affected. Where a river contains a significant component of treated sewage effluent and the nitrate concentration is high, then the result could be an increase in nitrate concentration of groundwater. In most cases, the contribution from this source is likely to be small compared to the agricultural inputs over the remainder of the catchment.

The other potential sources are likely to be relatively modest on an overall national scale, but could be important at the catchment scale. Significant leaching of nitrate may occur beneath the most intensively fertilized recreational turf areas, but these are likely to be a very small proportion of any catchment land area. Most recreational areas, such as school and council playing fields are likely to have more modest fertilizer applications. Airfield de-icing and landfills could be locally important, but are likely to be restricted to few catchments. The use of urea-based de-icing compounds is being phased out by civil airport authorities, partly on environmental grounds, and their usage at military airfields in NVZs may be discontinued by the Ministry of Defence.

KEY WORDS

Non-agricultural nitrate, point-source pollution, groundwater, river-aquifer interaction, unsewered sanitation, sewage sludge, sewer leakage, intensive farming, silage, slurry, airfields, sports turf.

1. INTRODUCTION

1.1 Background

The extent of groundwater pollution by nitrate in the United Kingdom has been well established in the last fifteen to twenty years. Nitrate has been identified and remains a major water quality issue, originating as a diffuse pollutant in all of the major aquifers and many of the minor aquifers of England and Wales. The important contribution that agriculture makes to the rise in groundwater nitrate concentrations has been demonstrated by research carried out by both the environmental and agricultural sectors in the 1970s and 1980s. Considerable scientific effort has been devoted to understanding and quantifying the behaviour of nitrogen inputs from normal agricultural practices, and their transport to groundwater. This situation is also encountered in other European countries, and the EC Nitrate Directive and AgriEnvironment Regulations have been developed as a community-wide approach to modifying farming practices to control nitrate leaching from agricultural soils.

Whilst these important European initiatives are strongly targeted on the arable farming community, there are other potential sources of nitrate which affect controlled waters. Some of these activities are completely non-agricultural, whilst others are non-arable agricultural, and most are poorly characterised and quantified at present. As a result, the Environment Agency (EA) could potentially be vulnerable to criticism from farmers, landowners and their representatives for taking a perceived partial and non-scientific approach to the implementation of new European legislation. Under the Nitrate Directive, review of Nitrate Vulnerable Zones (NVZs) and new candidate NVZs will be carried out every four years. The first review is due to be completed by the end of 1997, and the EA will be providing technical support to the UK government. Scientifically robust yet relatively simple methods need to be used for establishing a balanced perspective of the contributions from non-agricultural, non-arable agricultural and arable agricultural activities.

1.2 Objectives of Study and Scope of Report

The objectives of the study were clearly stated by the EA in the specification provided. The overall objective of the project is to gain a better technical basis for dealing with non-agricultural sources of nitrate, and to understand the nature and size of nitrate loadings and the pathways to groundwater of non-agricultural sources of nitrate. This improved knowledge will be used to guide the EA's approach to NVZ designation and review, and to assist in the implementation of other environmental legislation.

The specific objectives of the study are:

- To produce a focused literature review of quantitative studies of nitrogen loading and groundwater pollution from non-agricultural sources of nitrogen.

- To review hydraulic flow and nitrogen data from the losing reaches of rivers receiving effluent from sewage treatment works. This could provide indications of the extent and likely magnitude of the infiltration of nitrogen compounds where such reaches recharge aquifers which are extensively used for public supply.

- To identify and quantify nitrogen leaching from other sources.

- To produce case studies of representative catchments using the methods developed in the study.

- To produce a synoptic report bringing together the case studies with the reviews, and to draw conclusions and make recommendations which can be used to guide EA policy and to strengthen technically EA advice to relevant Government departments and other bodies.

The synoptic report forms R&D Technical Report P32. This report is the literature review component of the study. The following section lists the various non-agricultural sources of nitrate, and summarises the availability of information relevant to each. Reviews of each of the potential non-agricultural sources of nitrate listed below are given in the subsequent chapters, and a final chapter summarises them and indicates which are likely to be the most important. An extensive bibliography is included, as specified in the terms of reference.

Discussions with the EA project steering committee during the early stages of the project resulted in the issue of losing river reaches having somewhat lower emphasis in the overall project. Nevertheless, this topic was included for completeness in this literature review.

1.3. Potential Non-agricultural Sources of Nitrate

As stated in the introduction, agricultural sources of nitrate in water have been well characterised by a large body of research over the last twenty years. This applies to both cultivated and grazed farming land. There are a number of other potential sources of nitrate of which the more significant could include:

- urban or suburban areas, the recharge from which may include leakage from sewers and septic tank effluents

- infiltration of river-borne effluent from sewage treatment works in losing reaches of rivers

- application of sewage and other sludges to land (as a disposal practice)

- atmospheric deposition of nitrogen

- use of urea-based de-icing compounds at airfields

- recreational use of fertilizers in parks, golf courses and playing fields

- disposal/storage of wastes from intensive livestock farming

- landfill leachates
- highway drainage

1.4 Approach to Literature Review

A wide-ranging review was initiated using, amongst other sources, the BIDS on-line retrieval system. A list of some 270 references was obtained and has been installed in the PAPYRUS bibliographic database system. This was used to maintain an archive which was updated through the lifetime of the project. The current listing is reproduced as EA Project Record P2/i662/03, and is available to the EA on diskette. Many of these references were obtained through the British Geological Survey (BGS) library and the inter-library loan system.

This approach dealt reasonably well with the published scientific literature, but did not capture the unpublished material or work of research institutes and funding agencies. Approaches were made by letter, fax and telehone to colleagues in the US and within the EA, Water Research Centre (WRc), Department of the Environment (DoE), Ministry of Agriculture, Fisheries and Food (MAFF), Agricultural Development Advisory Service (ADAS) and other relevant UK organisations to address this issue.

Table 1.1 provides a summary of the published sources of information and the current and recently-reported research on non-agricultural sources of nitrate within the UK. The problem of differentiating between agricultural and non-agricultural sources of nitrate in groundwater has been widely recognised in the United States. Many farming areas in the US are characterised by the close proximity of agricultural sources, unsewered domestic sanitation and relatively shallow, private groundwater supplies, many of which are affected by high and/or rising nitrate concentrations. Nitrogen isotopes have been widely used to attempt to distinguish between agriculture and sanitation as the dominant nitrogen source in these regions.

Several of the potential nitrogen sources appear to have been little researched, and for some practically no published information is available (Table 1.1). An important gap in knowledge remains in relation to current European work; it can be anticipated that other EU member states will have had to deal with the issue of non-agricultural nitrate sources in their own national programmes for implementing of the Nitrate Directive. Personal contacts were pursued to try to locate relevant information from Europe, but with little success.

Table 1.1 Summary of existing information on nitrogen sources

Nitrogen Sources	Journal Publications			UK Research		Notes
	UK	EU	US	Completed	Current	
Atmospheric deposition	++	+	++	DoE (1994)	ITE.	Wet and dry
Land application of sewage sludge	++	+	++	FWR (1994)	MAFF, ADAS	Important
				Smith (1996)		
Losing rivers	++	+	+	Univ. Birmingham	Univ. Bradford	EPSRC/MAFF/NRA current contract
Septic tanks	o	?	+++		?	
Leaking sewers	+	+	o	Univ. Birmingham	Univ. Bradford?	Advance copy of CIRIA report obtained
				CIRIA (1995)		
Highway drainage	+	++	o	CIRIA (1994)	-	
Landfills				DoE (1996)	?	Not yet completed. Draft Aspinwalls copy
Recreational fertilizer use	+	?	+	Sports Turf Res Inst.	?	
Airfield deicing with urea	o	o	o	None	None	Decreasing problem due to replacement with glycol
Intensive livestock (pigs)	+	?	o	?	ITE?	Contributes significantly to atmospheric deposition
Silage clamps	o	o	o	?	?	Most common type of farm pollution
Slurry storage	o	?	+	ADAS/BGS (1994,97)	ADAS?	Bridgets Farm
Land application of treated effluent (ASR)	+	?	++	WRc (1984)	-	Phoenix, USA; Winchester, UK; Israel
Identification methods						
Stable isotopes	+	?	+++	Jersey	Univ. East Anglia	BGS and U Birm. Bradford and EA
Chemical tracers	+	?	?		Univ. Bradford	
Modelling	++	?	+	Univ. Birmingham	-	Bishop & Rushton (1993), Notts Trias

Notes: +++ plentiful, ++ few, + hardly any, o none, ? uncertain;
ITE Institute of Terrestrial Ecology
EPSC Engineering and Physical Sciences Research Council
FWR Foundation for Water Research
CIRIA Construction Industry Research and Information Association

2. UNSEWERED SANITATION AND LEAKING SEWERS

2.1 On-site Sewage Disposal

The use of on-site subsurface sewage disposal systems has long been recognised as one of the most effective means of dealing with domestic wastewater in rural settings. However, the build-up of nitrate in groundwater is recognised as potentially one of the most significant long-term consequences of this means of disposal. Such systems are not designed to produce high quality effluent, but the quality should be similar to that of effluent from primary sedimentation tanks at sewage treatment works.

There are thought to be 80,000 installations (septic tanks, cesspools and small sewage treatment plants) in England and Wales (Payne and Butler 1993). Most discharge at less than 5 m^3 per day and therefore do not automatically require an EA consent to discharge to land or underground strata. Of these, several thousand are likely to cause problems (backing up of sewage, environmental or water contamination), of which the majority are related to septic tanks. Problems are caused by blocked or inadequate drainage, and can be attributed to poor location, poor design or lack of maintenance. Drainage fields are not covered by Building Regulations, so unsuitable construction cannot be prevented. Cesspools are supposed to be watertight and those which are regularly emptied do not cause problems. The high cost of emptying can lead to deliberate damage to the seal to allow sewage to escape. There are no performance standards for small sewage trearment 'package' plants and most problems are thought to be caused by poor maintenance.

2.1.1 Septic tanks

Septic systems are designed to operate as follows. Raw sewage is fed to the tank and the liquid from settled sewage is discharged to a drainage field through the tank outlet. Three zones are present in a septic tank: a scum layer which forms a crust on the surface of the tank liquor, the wastewater and a bottom sludge layer of deposited material. This sludge accumulates and has to be periodically removed. The chemical evolution of effluent in unsewered systems is described by Wilhelm et al. (1994a,b). Organic matter contributes organic carbon and almost all the organic N to septic tank effluent. Originally the organic matter in domestic wastewater consists of approximately 40 - 50% proteins, 25 - 40% carbohydrates and 10% fat, but this organic matter can be altered by anaerobic digestion in the septic tank. This involves the hydrolysis of biodegradable organic molecules to smaller, more soluble components whicht are consumed during methanogenesis. Most N is originally bound in molecules such as proteins and urea. The total N content of the wastewater may be reduced by up to 30% due to organic N storage and denitrification in the sludge. Nitrogen is almost totally in reduced form when it leaves the septic tank. Measurements by Wilhelm et al. (1994) for septic tank effluents gave 32 mg/l NH_4 but only 1.3 mg/l NO_3. The ammonia was thought to represent about 75% of the total reduced N. The amount of anaerobic digestion which takes place depends on the size of tank, frequency of cleaning and temperature. However, in the UK temperatures are considered to be too low for any significant digestion to take place (Payne and Butler 1993).

The drainage field typically consists of either a soakaway, a system of sub-surface irrigation pipes or a tilefield. Insufficient attention is often given to the design and installation of the drainage field. The drainage system should be designed to allow for subsurface aerobic oxidisation of wastewater. The majority of N in the effluent is oxidised to NO_3 in the unsaturated zone and remains in an oxidised state in the saturated zone. The oxidation of NH_4 is an aerobic reaction that is microbially mediated. In well-aerated systems complete nitrification occurs within 0.5 m of the tilefield. Wilhelm et al. (1994a) found that NO_3 in the effluent at the water table represented 70% of the N originally measured in the effluent. The cause of this significant loss is not clear, but several possibilities exist.

Both organic N and NH_4 can be retained in the solid sludge. Organic N is retained when organic matter accumulates in the drainage field soils. NH_4^+ can be retarded by cation exchange reactions with negatively charged clay surfaces and is especially strongly bound by micaceous clay minerals. The accumulation of NH_4^+ in anaerobic soil was shown by Walker (1973a,b). NH_3 may also be lost by volatilisation of ammonia gas or via denitrification at anaerobic microsites in the unsaturated zone. The ability of some systems to retain N may initially be quite high but is likely to decrease over time as the exchange sites equilibrate.

In the saturated zone, both the development of anaerobic conditions and the process of denitrification are probably limited by the lack of labile organic carbon (Keeney 1986), since most of the organic carbon is removed from the wastewater as NO_3 is formed and before the effluent reaches the water table.

2.1.2 Cesspools

A cesspool is a water tight tank installed underground for the storage of sewage. No treatment is involved. Holding time is specified as at least 45 days and the minimum capacity should be 18 m^3. Cesspool liquors are very concentrated and usually in a septic condition. These systems are intended to be emptied frequently. Disadvantages of this type of system are the high emptying costs and the risk of escape of untreated sewage.

2.1.3 Package sewage treatment plants

This term is applied to a range of plants engineered to treat a given wastewater loading using prefabricated components and requiring a minimum of site work to install. They are often used for small housing complexes as opposed to single dwellings. Initial outlay and maintenance costs are higher than for septic tanks but they have several advantages: compact size, lower production of sludge and potential for extended sludge storage without odour nuisance. The most common type are activated sludge units where incoming effluent is contacted with aerated sludge to absorb the solids. The liquor is discharged and the sludge retained for collection. The quantity of nitrogen excreted per person is fairly uniform (2 - 3 kg/a) (Payne and Butler, 1993), but the resulting concentration in effluent depends on the rate of water consumption and hence the quantity of wastewater discharged. Quality information for untreated effluents is summarised in Table 2.1.

Table 2.1 Summary of nitrogen contents of domestic wastewater

Reference	Location	Wastewater discharge (l/person/day)	Typical N concentration (mg/l)	Sources	
				Black water	Grey water
Wilhelm et al. 1994a	Ontario	100 - 200	20 - 60	5 - 45% Toilet 70 - 90% urea and proteins	55 - 75% Kitchen, bath and laundry 10 - 30% NH_4 salts in cleaners
Hantzsche & Finnemore 1992	California		25 - 100 average 35 - 45 (75 - 80% NH_4)		
Porter 1980	Long Island	151	75		
Robertson et al. 1991	Ontario		31, 59		
Postma et al. 1992	USA	170	83 - 115		

2.2 Estimates of Impact

Robertson et al. (1991) describe two cases in which the impact of single septic tanks has been studied. At the first a well defined shallow plume, more than 130 m long and 10 m wide, was characterised by high Na, Cl and NO_3, and low DO. Due to high background concentrations of Cl and NO_3, Na was the best indicator. NO_3-N was present at up to 40 mg/l. The second site was similar although less extensive due to a shorter period of discharge. NO_3 was shown to be discharged to the river bed but was immediately removed by denitrification in the bottom sediments. This needs to be considered when assessing the impact of losing reaches of rivers.

The influence of the density of installations on water quality in the USA was reviewed by Bicki and Brown (1991) and a correlation between density and quality observed. Various estimates of the correlation between the density of septic tank discharges and nitrate concentration in groundwater have been made (Table 2.2). One of the factors responsible for the wide variation is the amount of nitrogen which is removed from the effluent by denitrification and sediments during retention in the tank. Estimates of this are shown in Table 2.3

Table 2.2 Relationship of unsewered sanitation density to groundwater nitrate concentration

Reference	Population density (persons/ha)	System density (unit/ha)	Average groundwater NO_3-N concentration (mg/l)	% of wells in area with NO_3-N exceeding 10 mg/l
Cogger 1988	12	-	8	-
Katz et al. 1980	25	-	-	25
Woodward et al. 1961	1.3 2.7	-	-	2 29
Geraghty and Miller 1978	-	<1.25 >2.8	-	<10 50
Morris et al. 1994	100-200	-	25-60	-
Gold et al. 1990	15	5	-	-

2.3 Leaking Sewers

The EA has taken an active stance on the presence of sewage works, foul sewers and storm overflows within source protection zones, as defined in Appendix H of the Policy and Practice for the Protection of Groundwater (NRA 1992). The laying of new main sewerage systems within Zone 1 is classified as an unacceptable activity. The onus is placed on developers, sewerage undertakers and their consultants to demonstrate that any proposed activity does not put groundwater resources at risk.

Table 2.3 Percentage of nitrogen from septic tanks leached to groundwater

Reference	Amount nitrogen produced (kg/person/year)	% of household output N leached to groundwater	% of holding tank effluent N leached to groundwater
Wilhelm et al. 1994	-	-	70
Brown et al. 1984	-	-	2.2, 0.7, 0.2
Morris et al. 1994	-	20 - 25	-
Walker et al.1973a	-	-	100
Robertson 1991	-	-	60 - 90
Gold et al. 1990	3.16	79	-

The most common defects in sewerage systems which might give rise to leakage during service are: cracks and fractures, joint displacement, root intrusion, deformation and collapse, reversed gradients, siltation or blockage and poorly constructed connections (Misstear et al., 1995). Few of these defects occur in isolation and a number may be present arising from a single cause. The primary causes may be, ground movement, ground loss or material deterioration. Eiswirth and Hötzl (1994) investigated the extent of damage in an old section of sewer using a TV camera. They found that this cannot distinguish between active and inactive sites and that hydrological, hydrochemical and geoelectrical methods were the most efficient. Combined flushing and tracer experiments were carried out to determine the preferred flow paths.

Leakage from underground sewers is a general problem in most cities of the world, but Lerner and Hoffman (1993) were only able to describe two documented cases of groundwater quality studies in sewered areas. They also identified ten published cases in the UK where groundwater pollution has been traced to leaking sewers. All of these involved microbiological pollution of public water supply sources. Of six other incidents communicated directly to these authors, only one was of another type.

Lerner and Hoffman (1993) found clear evidence of sewer leakage polluting the unconfined Triassic Sandstone under Nottingham, with elevated concentrations of chloride, ammonia, nitrate and other species. Under Birmingham, both industrial sources and sewer leakage were particularly evident in shallow samples collected under the city centre. Here, boron, nitrate, sulphate and phosphate were found. The best data set came from the Carboniferous Sandstone under Coventry, where elevated concentrations of TDS, boron, chloride, sulphate and chlorinated solvents were present (Barrett et al. 1995; Lerner and Barrett 1996). Leaking sewers were thought to be responsible for most of the inorganic loading.

Rettinger et al. (1991) describe a detailed study in the Quaternary sand and gravel aquifer underlying Munich. At the study site, sewage was disposed into the subsurface from a perforated underground pipe. They found it difficult to detect differences in water quality in a down gradient well using a pump to take samples because of the stratified nature of the pollution. Profiles from

a multilevel sampler were able to demonstrate high dissolved organic carbon (DOC), Zn, HCO_3, NO_3 and SO_4.
Andersson (1996) describes the use of tracers for leak location in sewers but this is confined to inward leakage from storm drains and water mains.

Misstear et al. (1995) attempted to draw links between characteristics of the sewer system and groundwater contamination from various incidents. It appeared that there was a steady rise in the number of incidents with age of the system. Pre-1936 sewers were responsible for some 50% of the incidents, having exceeded their design life. None of the incidents implicated sewers installed after the introduction of the Civil Engineering Specification for the Water Industry and of Sewers for Adoption in 1978. The most common cause was joint fracturing, resulting from the pre-1978 practice or using rigid joints without proper bedding. There was no evidence that pipe deterioration was responsible.

Of the 17 incidents reported to Misstear et al. (1995), only three were detected by observation of high concentrations of nitrate in a nearby borehole; the remainder were traced from bacterial contamination. They concluded that the best general determinands for defining sewer related pollution are bacteria, nitrate, phosphate and boron, but that isotopic studies are required to define the source accurately. Existing groundwater monitoring is inadequate to quantify the scale of sewer-related problems and detailed field studies are required to identify the precise extent.

Neames (1994) estimated the contribution of potential sewer leakage to nitrate in water abstracted from a source in the Isle of Thanet by calculating the potential losses from good integrity pipes but under unrealistically high water pressure. This corresponded to only 0.34% of the total sewage flux and was thought to be unrepresentative of point source leaks. Further calculations assuming sewer leakage in the range 2.5 - 10% suggested a maximum contribution of 0.36 mg N/l to nitrogen in the public supply. Extension of the 10% assumption to other sources in the Isle of Thanet is shown in Table 2.4. This indicates that sewer leakage is potentially responsible for significant concentrations of nitrogen in sources D and E where more than 60% of the catchment is urbanised.

Table 2.4 Sewer contributions to abstracted water based on urban area

Source	Annual abstraction (m^3/a)	Urbanised land area (km^2)	Equivalent pumped concentration due to sewage nitrogen (mg N/l)		
			2.5% leakage	5% leakage	10% leakage
A	1,367,700	0.82	0.25	0.50	1.00
B	1,978,400	3.82	0.81	1.61	3.22
C	598,800	0.92	0.64	1.28	2.56
D	181,200	1.48	3.41	6.81	13.63
E	384,800	2.28	2.47	4.94	9.88

After Neames (1994)

2.4 Methods for Estimating Nitrogen Leaching to Groundwater from Unsewered Sanitation

Hantzsche and Finnemore (1992) describe a simple method to predict nitrate impact over a defined area by constructing a mass balance considering only inputs from wastewater and rainfall recharge and losses due to denitrification in the soil column and the upper portion of the aquifer. The expression for the resultant average NO_3-N concentration, n_r, in groundwater is given by:

$$n_r = \frac{In_w(1-d)+Rn_b}{(I+R)}$$

in which I = volume of wastewater entering the soil averaged over the total gross developed area, in inches per year; n_w = total nitrogen concentration of wastewater, in mg/l; d = fraction of nitrate nitrogen loss due to denitrification in the soil; R = average recharge rate of rainfall, in inches per year; and n_b = background nitrate-N concentration in mg/l at the water table, exclusive of wastewater influences. This assumes uniform and complete mixing of wastewater and rainfall recharge over the entire area, which is completed by the time that the water table is reached. The equation can be converted into another form which is used to estimate the maximum density of septic tank units (or minimum lot size) that is necessary to keep nitrate concentrations below 10 mg/l. This has been applied to several areas in the USA and compared to actual field sampling data. It provided a reasonable first approximation and was felt to be an effective planning tool (Hantzsche and Finnemore 1992).

In areas where all of the population is using septic tank systems, estimates of nitrogen leaching and possible nitrate concentrations in groundwater can be made from the population density and hydraulic loading. An early attempt to do this was described by Lewis et al. (1980a), and compared with field observations of groundwater nitrate concentrations in large villages using pit latrines in Botswana. In that study, with population densities of some 60/ha using pit latrines in a region where the annual groundwater recharge was 50 mm or less, groundwater nitrate concentrations of up to 4 times the recommended guideline value of 11.3 mg NO_3-N/l were both predicted and observed (Lewis et al. 1980b).

Foster and Hirata (1988) estimated the load (C) from a diffuse source such as an urban or suburban area using unsewered sanitation with the equation:

$$C = \frac{1000aAf}{0.36AU+10I}$$

where a = unit weight of NO_3 or Cl in excreta (kg/person/year), A = population density (persons/ha), f = proportion of nitrogen oxidised, I = natural rate of rainfall infiltration (mm/year) and U = non-consumptive water use (l/person/day).

In applying this method, the greatest uncertainty surrounds the proportion of the nitrogen load that is oxidised and leached to groundwater. Ranges of 20 - 60% (f = 0.2 to 0.6) has been reported in the literature (Walker et al. 1973a, Kimmel 1984, Thompson and Foster 1986). The actual proportion oxidised and leached will depend on the per capita water use, the proportion of volatile losses of nitrogen compounds, and the amount of nitrogen removed during cleaning which will vary with the type of installations involved.

Morris et al. (1994) applied this method to the rapidly developing cities of Lucknow, India and Santa Cruz, Bolivia. In Lucknow, groundwater nitrate concentrations were generally between 25 and 60 mg/l, indicating that only about 20% of the nitrogen available from sanitation was being leached (Figure 2.1). Results from Santa Cruz indicated that a similar percentage of nitrogen was being leached, but with the lower population density and higher water use giving concentrations of 10 - 40 mg NO_3-N/l. A positive correlation between nitrate and chloride was also obtained. This was taken to indicate that they could both be largely derived from excreta. The weight ratio of chloride to nitrogen was approximately 2:1 in both cases. Since the average ratio in excreta is 1:2.5, this ratio is also consistent with only 20% of the nitrogen being leached to groundwater.

Island communities often employ in-situ sanitation systems using septic tanks because of the difficulty of disposing of collected, water-borne sewerage. These are often scenic tourist destinations where protection of the coastal environment is paramount, and disposal of sewage into

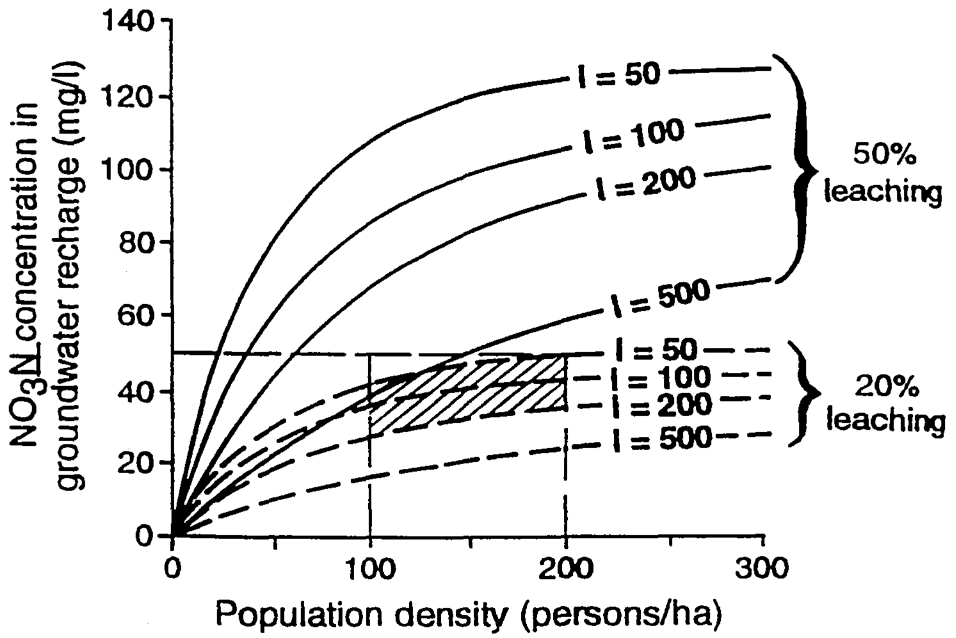

Figure 2.1 **Relationship of nitrogen leached to population density and infiltration beneath Santa Cruz, Bolivia (from Morris et al. 1994)**

near-shore seas is not desirable. The Channel Island of Jersey is typical in this respect. Eighty five per cent of the population, mostly concentrated on the south coast, have water-borne sewerage while the remaining 15% spread over the remainder of the island depend on septic tank systems. The island also has a highly-developed farming system; the impact of intensive cultivation and unsewered sanitation both occur in the same areas and distinguishing between the two became important in relation to the design of possible control measures (Chilton and Bird 1994). Groundwater nitrate concentrations are such that more than half of the samples exceeded 11.3 mg NO_3-N/l. Assuming production of some 3-4 kg N per person each year, the approximately 12,000 people using septic tanks would produce a loading of some 5 kg N/ha if spread uniformly over the 90 km^2 which constitute the rural part of the island. Taking a worst case, and assuming that all of the deposited nitrogen is oxidised to nitrate and mobilised, then the annual groundwater recharge of only 50 - 100 mm would contain nitrate at concentrations of up to 6 - 8 mg NO_3-N/l. Even though locally the rural population density and nitrogen loadings may be somewhat higher, this would be offset by the fact that only a proportion of the nitrogen is likely to be oxidised and leached to groundwater. The authors suggested that nitrogen originating from this source was unlikely to have a significant impact on groundwater quality when compared to intensive agriculture (Chilton and Bird 1994), and this was subsequently supported by nitrogen isotope analyses (Feast 1995).

A similar situation exists on the Caribbean island of Barbados (Chilton et al. 1991). Many of the rural and suburban population use septic tanks for domestic sanitation. Widespread cultivation of sugarcane with moderate applications of nitrogen fertiliser produces groundwater nitrate concentrations in the range of 6 - 8 mg NO_3-N/l over much of the island. In the rural areas, population densities of some 4 persons/ha generate a nitrogen loading of about 20 kg N/ha/a. With per person water consumption of some 250 l/person/day and annual infiltration of some 350 mm, nitrate concentrations in the resulting recharge would be some 5 mg NO_3-N/l, if all of the nitrogen were oxidised and leached. In the more densely populated suburban areas (31 persons/ha), nitrate concentrations in groundwater recharge of up to 25 mg NO_3-N/l have been observed. Regular monitoring of groundwater quality confirmed the presence of higher nitrate concentrations in the more densely populated suburban areas. In this study, the non-agricultural origin of these local high nitrate concentrations was confirmed by the associated presence of regular and high faecal coliform counts (Chilton 1991), which were not widely observed in the more rural areas. The population density, especially in the suburban area, is much higher than in Jersey, producing a higher nitrogen loading, which is partly offset by the greater recharge.

Bauman and Schafer (1984) present a model based on the work of Mercado (1976). This attempts to represent the groundwater system as a single cell applicable only to isotropic and homogeneous aquifers. It makes similar assumptions to Hantzsche and Finnemore (1992) and also assumes that all nitrogen from the effluent is transported to the water table. The authors state that given the limitations in the quantitative data available, such assessments are as much an art as a science and depend on the skill of the appraiser.

3. HIGHWAY DRAINAGE AND SUBURBAN RUNOFF

3.1 Highway Drainage

The earliest concerns about groundwater pollution from highway drainage relate to the application of de-icing salts in winter in Europe, Canada and the northern parts of the US. Increased concentrations of sodium and chloride were attributed to heavy applications of salt, and an example from Massachusetts of the rapid rise and subsequent response to the local restriction of use is shown in Todd (1980). If traditional rock salt were replaced by urea compounds, then nitrate could replace chloride as the major contaminant of affected groundwater (see below).

Information about the discharge of highway drainage to surface and groundwater in the UK is largely anecdotal. Generally, no effects on quality are seen from annual average daily traffic (AADT) of less than 15000, and only minor effects have been identified from AADT between 15000 and 30000 (Maestri et al. 1988, Ellis and Revitt 1991). Only heavily-trafficked main roads, urban distributors, trunk roads and motorways require specific interception and drainage measures. Table 3.1 shows the loadings of nitrogen as ammonium, in kilograms per hectare per year, obtained from highway runoff of various ranges of AADT from the UK, USA and Germany in the 1970s and 1980s.

Table 3.1 Annual loading of nitrogen as ammonium from highway traffic

Highway type	Average annual daily traffic	NH_4-N (kg/ha/a)	Study area	Study dates	Source of data
various urban	< 30000	3.6	USA	1976 - 77	US-FHA (1981)
rural motorway	41000	4.6	Germany	1978 - 81	Stotz (1987)
rural motorway	47000	3.2	Germany	1978 - 81	Stotz (1987)
various motorway	> 50000	3.3	UK	1980s	Ellis and Revitt (1991)

From Luker and Montague (1994)

The worst cases of highway runoff pollution occur due to short duration intense summer storms which generate a small total quantity of rainfall after a long antecedent dry period. Pollutants that have accumulated during the dry period are mobilised by the high intensity rainfall and discharged into streams that are likely to be in low flow conditions. The storms may cause a double peak of pollutants; firstly those included as sediments in the drainage system deposited after previous runoff events, followed by material which has accumulated on the road surface. Table 3.2 gives ranges of nitrate and nitrite and total nitrogen measured in runoff from various road types (an explanation of the subgrouping of road types was not given). Sources of nitrogen in highway runoff that include, or could subsequently form nitrate are: sediments; exhaust emissions; urea as a de-icing agent; and accidental spills. These are summarised in turn.

Table 3.2 Reported ranges of nitrate and nitrite and total nitrogen concentrations, in mg/l, measured in runoff from various road types

Pollutant	Rainfall concentration	Motorway		Urban			Rural
		I	II	I	II	III	
Nitrate & nitrite	0.01 - 5.0	-	-	0.3 - 6.9	-	0.4 - 1.5	0.2 - 0.9
Total nitrogen	0.5 - 9.9	-	1.4 - 3.3 (av. 1.8)	0.2 - 14	0.2 - 1.0	1.0 - 3.2	0.3 - 2.2

From Luker and Montague (1994) using Colwill et al. (1985), Strecker et al. (1990)

3.1.1 Sediments

Sediments on highways are usually associated with the everyday passage of traffic. They consist mainly of products of abrasion from tyres and paved surfaces, corrosion of vehicles and their components, fuel and lubricant losses and vegetation. Hvitved-Jacobsen et al. (1986) found that 85 - 90% of nitrogen nutrient loading in drainage water was removed with sediment. They suggested that if sediments are removed effectively from the drainage water then problems are unlikely. Further, Collins and Ridgeway (1980) found that very fine particles, which constitute only 6% of the total sediment but are more easily mobilised, contain from 30 to 50% of all nutrients, including N.

3.1.2 Exhaust emissions

Nitrogen oxides are known to be emitted from vehicle exhausts. Exhaust emission contributes to runoff pollution when taken-up by rainfall or snow and returned to the road surface as a component of atmospheric deposition. As many of the pollutants from highways are directly associated with road traffic, they will have increased concentration where traffic density is higher. However, the proportion of nitrate pollution from emissions is reported to be small (Luker and Montague 1994).

3.1.3 Accidental spillages

The risk of nitrate pollution exists from accidental spillages from lorries carrying loads such as inert slurries and sewage sludge and is not likely to be significant. Price et al. (1989) calculated the risk of accidental spillage at interchanges as over twice that at intermediate road sections.

3.1.4 Urea as a deicing agent

Though the most common method of road deicing is still the use of rock salt, trials of other less corrosive agents such as urea have been made on more vulnerable sections of highway. Urea is a source of nitrogen as it hydrolyses to ammonia, which subsequently oxidises to nitrate (see Chapter 10).

3.2 Roof Areas

Roof runoff is generally found to be less contaminated when compared with other types of storm and waste water, particularly for nitrate.

3.3 Residential and Public Amenities

The type and concentration of pollutants in residential areas is dependent on the density of housing, the number and use of roads and the area of garden or grassland. One major source of nitrate is human waste, both as treated discharges to rivers and through leaking sewers (see section 2.3). Another major source is vegetative litter and garden fertilizer. The quantification of pollutants entering stormwater from this source is difficult as the loading is intermittent and varies seasonally.

Though referring to urban environments, Makepeace et al. (1995) present concentrations of nitrogen found in stormwater (Table 3.3). They suggest, in general, that nitrate from this source is a minor problem for humans but a major one for some aquatic life.

Table 3.3 Forms of nitrogen and their concentrations in stormwater

Form of nitrogen	Concentration (mg/l)
Total nitrogen	0.32 - 16.00
Inorganic nitrogen	0.09 - 5.44
Organic nitrogen	0.32 - 16.00
Nitrate-N	0.01 - 12.00
Nitrite-N	0.02 - 1.49
Ammonia-N	0.01 - 4.30
Total Kjeldahl nitrogen	0.32 - 16.00

From Makepeace et al. (1995)

3.4 Comparative Levels of Nitrate Pollution

Table 3.4 gives concentrations of total nitrogen originating from several sources for Denmark (Mikkelsen et al. 1994). The values for highway runoff here are low compared with many investigations; this is due to the relatively low traffic density in Denmark. These concentrations are low compared with those in other types of polluting waters.

Table 3.4 Characteristic concentrations of total nitrogen (mg/l) in different types of urban runoff in Denmark

Urban runoff[1]	Highway runoff[2]	Roof runoff[3]	Atmospheric deposition[*]
2	1 - 2	<1	70%

Notes:
[1] PH-Consult 1990
[2] Hvivted-Jacobsen et al. 1992
[3] Malmquist 1982
[*] percentage of total nitrogen arising from atmospheric deposition and attached to particulate matter

From Mikkelsen et al. (1994)

4. FERTILIZER APPLICATION TO RECREATIONAL GROUND AND ALLOTMENTS

4.1 Fertilized Recreational Grounds

Fertilizer application to sports turf has a significant effect on the playing characteristics of the surface as well as its aesthetic appearance. Sports turf falls into the two main categories of fine and coarse turf. The former is used for golf greens and tees, croquet lawns, bowling greens, cricket pitches and tennis courts. Coarse turf grass is used for football, rugby and horse racing. The different demands on the two types of turf are reflected in the species of grass used and the fertilizer requirements. Fertilizer treatment can influence the ability of the turf grasses to withstand the stress from close mowing, and to resist fungal infection and minimise infestation by weeds.

Fertilizer applied to sports turf, parks and gardens may result in nitrate leaching, particularly if the ground is over-irrigated. Exner et al. (1991) investigated the impact of applications of ammonium nitrate to turf at rates of 0, 10, 15, 20 and 24 g/m^2 N (0, 2, 3, 4 and 5 times those recommended for a single application of nitrogen). The turf was irrigated every third day with an average of 51 mm of water during each irrigation event (more than three times the evapotranspiration rate). Analysis of the soil water showed that as much as 95% of the nitrogen applied in late August leached below the root zone. Average nitrate concentrations in the pulse ranged from 34 to 70 mg NO_3-N/l. Relatively uniform concentrations of 8 mg NO_3-N/l were also found below the unfertilized plot, reflecting the nitrate concentration of the irrigation water which was from the public supply. This indicates that it is important to consider the nitrate in the irrigation water as an available source of nitrogen for the grass.

The above investigation indicates the possibility of nitrate leaching where turf is over-fertilized and over-irrigated. Management practices which have led to high rates of nitrate leaching include: application of excessive quantities of nitrogen (Brown et al. 1977), use of highly soluble nitrogen compounds (urea, ammonium nitrate, ammonium sulphate or potassium nitrate (Synder et al. 1984)), use of nitrogen fertilizer in a dormant or semi-dormant period of limited plant uptake (Petrovic et al. 1989, Synder et al. 1984), and excessive irrigation (Synder et al. 1984, Brown et al. 1977, Morton et al. 1988). Although there is the potential for nitrate leaching from turf, providing fertilization is properly managed, nitrate leaching should not make a major contribution to groundwater nitrate concentrations (Petrovic 1989; Cohen et al. 1990). Turf fertilization practices, such as frequent light applications of nitrogen and lack of applications in autumn and winter when the grass is not growing, are likely to result in lower proportions of nitrate leaching from turf than from agricultural land. Research has been conducted into fertilization practices for sports turf which will minimise leaching (Lawson 1989, Lawson and Colclough 1991). Some of the results of this work are described below.

4.1.1 Fine turf

Fertilizer requirements vary according to the use of the turf. Golf greens and bowling greens have to withstand a large amount of foot traffic, and larger nitrogen uptake allows the grass to recover quickly from wear and tear. Thus the nitrogen application rate is normally within the range 110 to

200 kg/ha. On tennis courts and cricket pitches where dense rooting is encouraged and lush top growth discouraged, the annual nitrogen application rate is 80 to 120 kg/ha. This annual amount is normally applied in three to four dressings during the growing season, with the final dressing in late August having a relatively small nitrogen content.

For golf courses, there has been a trend towards the use of root zone constructions consisting mainly of sand, in order to provide free drainage. Because of this use of root zones with large hydraulic conductivities and small cation exchange capacities there has been an interest in the use of synthetic slow-release nitrogen fertilizers for fine turf to reduce leaching losses. Possible materials are isobutylidene diurea (IBDU) and urea-formaldehyde products. These have been shown to result in smaller leaching losses than those from inorganic fertilizers when applied to turf with root zones having a high sand content (Brown et al. 1982, Cohen et al. 1990). Another possibility is the use of nitrification inhibitors, such as dicyanide, for fine turf fertilizers. However, it is unlikely that the inhibition of the conversion of ammonium to nitrate would be effective in diminishing leaching losses in pure sand root zones with small cation exchange capacity, at least until an accumulation of organic matter had taken place.

Lawson and Colclough (1991) considered that, at annual fertilizer application rates of up to 200 kg N/ha, the concentration of nitrate found in drainage water would be unlikely to exceed the EC limit for drinking water if a dense grass cover is present. Even at an excessive application rate of 400 kg N/ha, the amount of nitrogen lost during the main growing season is small, but considerable nitrate leaching will occur in the autumn. Individual fertilizer dressings up to 50 kg N/ha can be applied without an immediate subsequent loss of nitrate through leaching. It is difficult to determine whether this is due to uptake of nitrogen by the turf grass, immobilisation in soil, or volatilisation. There has been little investigation into the extent of nitrogen loss from the soils under sports turf by means other than leaching, such as denitrification and volatilisation.

4.1.2 Coarse turf

Canaway (1984) studied the effects of nitrogen application on turf treated with ammonium nitrate, on both pure sand and sandy loam soil root zones. It was found that the optimum nitrogen application rates for the maintenance of ground cover on both root zone types lay between 200 and 300 kg N/ha per year. Measurements of shear strength at the surface of both sand and soil root zones indicated that the best playing surface was provided by a fertilizer application rate of 225 kg N/ha/a.

The quality of the turf and the amount of nitrogen fertilizer needed depend on the requirements of the user. In general, on local council sports fields the grass clippings are returned so that the fertilizer requirement is low. This contrasts with high class football and rugby pitches where clippings are boxed off in order to provide a firm surface, and a significant proportion of the nitrogen is removed. Recommended nitrogen fertilizer application rates for both turf types are summarised in Table 4.1.

Table 4.1 Annual nitrogen fertilizer rates for sports turf (kg N/ha/a)

Turf type	Use	Clippings	Root zone type	Nitrogen application (kg/ha/a)
Fine	Golf tees and greens	-	Soil	80 - 200
	Bowling greens		Sand	250
	Golf fairways			
	Cricket tables	-	-	80 - 120
	Tennis courts			
	Cricket outfields	Removed	-	80 - 120
		Returned	-	40
	Hockey pitches	Removed	-	80 - 200
		Returned	-	40 - 50
Coarse	Winter games turf	Removed	Soil	160 - 200
			Sand	250
		Returned	Sand	80 - 100
	Race courses	-	-	80 - 100

From Lawson 1989, Lawson and Colclough 1991

4.2 Gardens and Allotments

Leaching from domestic gardens is likely to be highly variable. The work by Exner et al. (1991) referred to above is intended to simulate an urban lawn, but was probably more heavily fertilized and irrigated than the average domestic lawn in the UK. Likewise the limited literature on vegetable growing, such as Pionke et al. (1990), is applicable to extensive irrigated commercial horticulture in a warm climate with dry summers.

5. ATMOSPHERIC DEPOSITION

5.1 Introduction

Although 78% of the earth's atmosphere is nitrogen, it is in the chemically inert gaseous form of N_2. However, nitrogen is emitted to the atmosphere from various sources in oxidised (NO_x) and reduced (NH_x) forms, the most important of which are nitric oxide (NO), nitrogen dioxide (NO_2), ammonia (NH_3) and nitrous oxide (N_2O). Oxidised nitrogen species are almost entirely generated by motor vehicles and industry, whereas the sources of reducing species are almost entirely agricultural. Nitrogen is also deposited in a variety of forms, and can undergo various interactions and transformations in the atmosphere, which makes the prediction of nitrogen deposition a complex process. Emission and deposition of nitrogen in its various forms has been quantified by the UK Review Group on Impacts of Nitrogen Deposition on Terrestrial Ecosystems (DoE 1994).

5.2 Nitrogen Emissions

5.2.1 Oxidised N (NO_x)

Emissions of NO and NO_2, jointly termed NO_x, arise both from human activity and natural processes. Nitrogen emissions for the UK in 1990 totalled 846,000 tonnes (DoE 1994). The major UK source of NO_x is the burning of fossil fuels by motor vehicles and power stations. Emissions from motor vehicles have risen rapidly since 1970 and now account for just over half the total with power stations contributing a further 28% (Gilham et al. 1992). NO is also emitted from soil (Johannsson and Gabally 1984), as it is produced by nitrification (oxidation of NH_4^+ to NO_3) and denitrification (reduction of NO_3^- to N_2O or N_2). The ratio of NO to N_2O emitted is influenced by the degree of aeration of the soil, with low rainfall stimulating NO production. NO can also be absorbed by soils. Emission of NO increases with increasing soil temperature and is greatest shortly after the application of nitrogen fertilizer.

5.2.2 Nitrous oxide (N_2O)

N_2O is produced by denitrification and ammonium oxidation in soil beneath fertilized land, woodland and semi-natural habitats, and by the industrial production of adipic acid. Emissions from the combustion of fossil fuels are relatively minor. Total UK emission is between 100,000 and 115,000 tons per year; relative contributions are summarised in Table 5.1.

Table 5.1 **N_2O emissions from the UK**

Land use	N_2O-N (kt N/a)
Fertilized land	22 - 36
Livestock waste	12
Forest and woodland	5
Semi-natural land	6
Road transport	3
Industry	49
Other fuel combustion	2
Total	**100 - 115**

From DoE (1994)

5.2.3 Ammonia (NH_3)

Ammonia emissions arise mainly from agriculture, particularly livestock farming and animal wastes. Emissions from livestock derive mainly from the decomposition of urea and uric acid in animal and poultry wastes. Emissions occur from housed animals, storage of manure and slurries, land-spreading of wastes and from animals grazing in the field. The largest source is thought to be land-spreading of wastes. There are many uncertainties involved in estimating NH_3 emissions, because of the range of agricultural practices and variable soil and meteorological conditions. Other sources of NH_3 include human emission, emissions from sewage sludge and industrial sources (especially fertilizer production). Total emission of nitrogen has been estimated at 180,000 to 440,000 tonnes per year by recent authors (ApSimon et al. 1987, Kruse et al. 1989, Ryden et al. 1987, Whitehead 1990, Jarvis and Pain 1990, Asman 1992, Eggleston 1992, Sutton et al. 1994). It is thought likely that emissions lie towards the upper end of this range at 310,000 to 400,000 tonnes per year (DoE 1994).

5.3 Nitrogen Deposition

Chemical transformations of nitrogen species in the atmosphere have significant consequences for their transport and removal. For example, oxidation often leads to more soluble species which are readily removed in cloud and rain droplets, and converts reactive gases to aerosol forms which are less readily dry deposited. The deposition of nitrogen from the atmosphere occurs as wet deposition of NO_3^- and NH_4^+, cloud water deposition of NO_3^- and NH_4^+ and the dry deposition of NO_2, HNO_3 and NH_3, and NH_4-SO_4 particles .

5.3.1 Wet deposition

The major ions in precipitation, which include NO_3^- and NH_4^+, are monitored throughout the UK using a network of collectors. The estimates of annual wet deposition are obtained as the product of the precipitation-weighted annual mean ion concentrations obtained from this network and the annual precipitation obtained from the Meteorological Office rainfall maps. The largest rainfall-weighted concentrations of NO_3^- and NH_4^+ are in East Anglia, with concentrations of 40 to 60 µeq/l NH_4^+ and 35 to 50 µeq/l NO_3^-(DoE 1994). Concentrations decline towards the west and north from this region with concentrations in West Wales and Cornwall in the range 15 to 30 µeq/l for both ions.

In combining the precipitation and concentration fields to obtain a wet deposition map for the country, a correction must be made for the effect of altitude. The precipitation collector network is located primarily on low ground for practical reasons; however, precipitation is highest on the higher ground. The additional precipitation at high altitude washes out cloud droplets from orographic (hill) cloud, which has approximately twice the concentration of major ions. This leads to a larger increase in wet deposition with altitude than that due to the increase in rainfall alone.

The wet deposition map of NO_3^- and NH_4^+ (Figure 5.1) shows the largest wet deposition of both ions in the high rainfall areas of Wales and north-west England. The total annual wet-deposited nitrogen for the UK is given by DoE (1994) as 108,000 tonnes of nitrogen as NO_3^- and 131,000 tonnes as NH_4^+.

5.3.2 Cloudwater deposition

Droplets of water in hill cloud are captured as they collide with vegetation. Work by Gallagher et al. (1992) indicates that rates of cloudwater deposition are of the same order as wet deposition. It is a particularly important input for NH_4^+ and NO_3^- for forested land above 400 m. The occurrence of hill cloud in Britain has been quantified by Weston (1992) and has been used to model the annual inputs from cloudwater deposition throughout the UK by Fowler et al. (1993). The annual amount of nitrogen deposited in this way is 2400 tonnes of nitrogen as NO_3^- and 2700 tonnes as NH_4^+.

5.3.3 Dry deposition

NO_2

NO_2 is deposited on vegetation; the primary sites of uptake are stomata (Hanson et al. 1989, Hargreaves et al. 1992) and uptake is seasonally dependent. Fowler et al. (1994) modelled the NO_2 deposition to vegetation at hourly time intervals, dividing the land-use of the UK into five classes: arable cropland, permanent grassland, hill vegetation, forest and urban. The proportion of

land in each of these classes was estimated for each 20 x 20 km grid square. There is considerable spatial variability within each grid square, reflecting the difference in NO_2 uptake for each land class; however, some variability is lost in the process of summing the annual deposition for each square. The NO_2 deposition to individual squares varied from 0.5 kg N ha/a to 7.2 kg N ha/a with a mean of 3.1 kg N ha/a. The total dry deposition of NO_2-N in the UK is approximately 107,000 tonnes N/a, which is very similar to the annual wet deposition (108,000 tonnes N/a) but with a very different distribution spatially and in time.

NH_3

Very large rates of NH_3 are deposited to moorland and forests. Over agricultural land, the annual deposition of NH_3, which takes place throughout the winter and when the crop surface is wet, is thought to be balanced by the emission of NH_3 during senescence and after the application of fertilizer. The estimation of dry deposition is therefore limited to woodland, moorland, hedgerows etc. (Figure 5.2).

5.3.5 Total deposition

Total nitrogen deposition is shown in Figure 5.3. This is highest over the Pennines and South Wales and with the majority of England receiving 15 - 25 kg/ha/a for the period 1989 - 1992.

5.4 Nitrate Leaching

Nitrogen introduced to land through atmospheric deposition is a relatively minor source of nitrate compared to agricultural fertilizers, which introduce about 3 - 5 times as much NO_3^-. Deposition is relatively more important where land is in set-aside or farmed organically. The extent to which atmospheric deposition will contribute to nitrate leaching depends partly on the form in which it is deposited; any deposited NO_3^- in excess of plant demands can move easily through the soil and increase NO_3^- concentrations in leachate. Atmospheric inputs of NH_4^+ may be immobilised in the soil before uptake or nitrification occurs. However, the system has a limited capacity to immobilise or utilise N, and when this is exceeded "N saturation" occurs and much of the added N appears in soil solution and is available for leaching.

Leaching of significant amounts of NO_3^- has been reported from forest systems in a number of areas of Europe; for example, the Harz Mountains and the Black Forest in Germany, the Vosge area of north east France, the Ardenne in Belgium, the Erzegebirje in the Czech Republic and the plantation forests in Wales (Anderson 1986, Emmett et al. 1993). Mineral N from internal sources plus atmospheric inputs are clearly present in these systems at amounts exceeding the demands of the biological system, causing N saturation. The enhanced leaching at the Welsh sites is age related, only occurring in older (> 35 years) plantations, and is probably related to reduced demand in older trees. Leaching losses of between 5 and 15 kg N/ha/year were shown for English forests overlying

the Chalk aquifer with considerably higher losses under beech plantations (up to 35 kg N/ha/year) where there is no understorey to consume the nitrogen (Kinniburgh and Trafford 1996).

6. LAND APPLICATION OF SEWAGE SLUDGE

6.1 Background

About 30 million wet tonnes of sewage sludge are produced each year (MAFF 1993), and disposal of this large amount is an important responsibility. There are three options for disposal of sludge: to land, to sea, and by incineration. The pattern of disposal varies between different regions of the country. EC regulations coming into force in 1997 will prevent disposal in the North Sea, which is likely to cause an increase in land disposal of sludge. Application of sludge to land is regulated under EC Directive 86/278/EEC (Council of the European Communities (CEC), 1986). Sludge may be applied to cultivated land, disposed of in landfills or used in land reclamation schemes. As well as providing a means of disposal, sewage sludge applied to agricultural land has value as a fertilizer. Currently, about 60% of sludge disposed to land is applied to agricultural land. This amounts to around 40% of sewage sludge produced (MAFF 1993). Less than 1% of agricultural land receives sludge.

Nitrate leaching from sewage sludge can be controlled in a similar way to nitrate leaching from inorganic fertilizers, for example by management practices such as winter sowing and restriction on timing and rates of application for the various sludge types. Shepherd (1994) recommends that application limits should be based on a sludge's total N content rather than its NH_4-N content, to avoid over-application of a sludge with low NH_4-N and high organic nitrogen. The Sludge (Use in Agriculture) Regulations (1989) apply to spreading of sewage sludge onto agricultural land, and are supported by a Code of Practice. Sludge or organic manure applied to land should not contain more than 250 kg/ha/a total N. The MAFF Code of Good Agricultural Practice for the Protection of Water (MAFF 1991) advises against application of organic manures with high available N content, including liquid sewage sludges, poultry manure and animal slurries, to arable land during autumn or early winter. Organic manures low in available N, such as farmyard manure and dewatered sludges, can be applied at any time. Sewage sludge used for agricultural benefit will be controlled by the measures covered by the MAFF code within NVZs and is not considered to be an issue.

Wastes arising from other activities may contribute nitrogen but there is little published evidence. In the future properly qualified advice will have to be presented by operators which will include compositional information. In Nitrate Sensitive Areas, application of organic manure (including sewage sludge) is limited to 175 kg/ha total N per year. Slurry and sludge should not be applied within 50 m of a spring, well or borehole that supplies water for human consumption. Organic manure produced by livestock also has fertilizer value, and many farmers dispose of their manure to agricultural land. However this does not fall within the scope of the present review.

Under the Agency's Policy and Practice for the Protection of Groundwater, application of sewage sludge (and farm wastes) for any purpose is not acceptable in Source Protection Zone I areas of supply catchments but may be acceptable in Zones II and III. Application of higher risk sludges is further restricted, and is normally not acceptable on aquifer outcrops.

6.2 Treatment of Sewage Sludge

The EC Directive on application of sludge to land states that all sludge must be treated prior to its use on farmland. Raw sewage sludge can be treated by digestion, either aerobically or anaerobically. Digestion reduces the bulk and destroys the offensive smell of raw sludge, and improves the properties of sludge as a fertilizer. Anaerobic digestion also produces methane gas which can be used as a source of energy. The majority of the sewage which is disposed of to land in the UK is treated by anaerobic digestion; a small proportion is treated by aerobic digestion (Aitken 1995). Liquid sewage sludge is often dewatered by pressing to give a solid sludge cake with about 25% dry matter or thermally dried into granules or powder with 95% dry matter. The cake form is particularly useful as a soil substitute in land restoration schemes. Cement kiln dust (CKD) treated sludge is produced by adding dewatered sludge to an alkaline mixture composed of cement kiln dust and other alkaline products. Composting sewage sludge for use in horticulture has not proved popular in this country because of the large land area required for the process, but is more widely used in other countries.

6.3 Nitrogen Content of Sewage Sludge

The proportion of nitrogen present and the chemical forms in which it occurs in sewage sludge depend on the sewage treatment process and subsequent treatment of the sludge. Analyses of sludges by the DoE (1981) gave a range of total nitrogen from 0.6 to 8.2 % of the dry solids. The mean and median values were 3.7 and 4.1 %, respectively. Korentajer (1991) reports median values of 2.9% (dry weight) N for sludges analysed. Around 15 000 tonnes of nitrogen is applied to agricultural land in the form of sewage sludge each year (MAFF 1993).

Unlike most purchased fertilizers, nitrogen in sewage sludge is present in both organic and inorganic forms. Nitrogen in undigested sludge is predominantly in the organic form. The digestion process converts more than half the total nitrogen into soluble forms, most commonly in the form of ammonium-N. The proportion of NH_4^+-N in sludge varies widely, from 5 - 60%. The concentration of nitrate is low due to the prevalence of anaerobic conditions which inhibit nitrification (MAFF 1993). When sludges are dewatered much of the nitrogen in soluble form is removed, so that both the proportion of nitrogen and its availability are reduced. Loss of nitrogen from undigested sludge is small, but that from digested sludge can be substantial, depending on the degree of dewatering. Typical concentrations are given in Table 6.1.

6.4 Nitrogen Leaching

Nitrogen in undigested sludge is predominantly in organic form, which must be transformed into inorganic nitrogen by mineralisation before it is available for plant uptake or leaching. The extent and rate of this process depends mostly on the composition of the sludge, soil and weather conditions. Mineralisation is more likely to occur in the spring and autumn when the soil is warm and moist. Any mismatch between the rate of mineralisation of organic nitrogen and the nitrogen

Table 6.1 Typical nitrogen content of sewage sludges by wet weight

Sludge type	Dry matter (%)	Total N (%)	Available N in first year (%)
Liquid undigested	5	1.8	0.6
Liquid digested	4	2.0	1.2
Undigested cake	25	7.5	1.5
Digested cake	25	7.5	1.1

Source: Hall et al. 1986, WRc 1985

demand of the growing crops will lead to the possibility of nitrogen being leached. Organic nitrogen is mineralised to NH_4^+-N, which, being positively charged, may be adsorbed to the soil, and is also subject to transformation to nitrate by nitrification. Nitrate is negatively charged, so if it is not removed from the soil by actively growing crops, it may be subject to leaching.

Sludges which have a high content of inorganic nitrogen relative to organic nitrogen, such as digested sludge, will have a much greater proportion of their N available in the first year for uptake by plants or for leaching. For sludges which have a high organic nitrogen content, the proportion of N available depends on the rate of mineralisation. Sommers et al. (1981) estimate the rate of mineralisation of organic nitrogen for the first year after application as 40% for unstabilised and waste-activated sludge, 30% for aerobically-digested sludge, and 10% for composted sludge. DoE (1981) suggest 20 - 35% of nitrogen from undigested sludges is available to crops in the first season after application. This is consistent with the estimates of availibility given in Table 6.1. Where undigested sewage sludge is applied to land over successive years, the available nitrogen will increase due to residual effects from decomposition of organic nitrogen from previous applications. For digested sludge, particularly in liquid form, the residual effect will be much smaller.

The availability of nitrogen from sludge is affected by immobilisation of N through uptake by soil micro-organisms, converting it into the organic form and making it unavailable for plant uptake or for leaching. The rate of immobilisation is affected by the carbon to nitrogen ratio of the sludge. In some recent studies, over a relatively short period (33 weeks), immobilisation and mineralisation were approximately in balance for slurries with a C:N ratio of about 20:1 whereas higher ratios resulted in a net immobilisation of nitrogen (MAFF 1993).

Other factors which affect the rate of nitrate leaching include the climate (temperature and rainfall), the method of sludge application (injection or spreading), the time of application, the soil type and the crop type:

- The risk of groundwater pollution is at its greatest following autumn applications when the soil remains warm enough for nitrification to take place and when there is usually no crop present to use the nitrate.

- Injecting sludge into the soil causes higher leaching losses than surface applications (FWR 1994); this is partly due to reduction of nitrogen loss by volatilisation of ammonia, which is greater when sludge is surface-spread.

- Arable crops remove most nitrogen from the soil in the spring and summer. Nitrate accumulated in the soil in the late summer and autumn is therefore susceptible to leaching loss by winter rainfall because there is insufficient crop cover of the soil to retain the available N. In contrast, grass provides a permanent cover and absorbs most of the N which has been mineralised.

- Leaching losses are greater from sandy soil, through which infiltration of rainfall rapidly occurs, than from clay soil.

Field estimates of nitrate leaching from sludge-treated land are highly variable (Tables 5.2 and 5.3), as the extent of nitrate leaching depends on many factors (sludge type, application time and method, cropping, soil type, climate). Experimental factors (for example spacing and depth of lysimeters) may also affect the estimates. Estimates of nitrate leaching have also been produced by modelling (Crohn and Haith 1994, Jansson et al. 1989). O'Brien and Mitsch (1980) estimated that the nitrate leaching rate increases by 21 kg N/ha/a per tonne of digested sludge (dry solids) applied to agricultural land. Assuming 200 mm of effective rainfall, this value equates to an average concentration in groundwater recharge of 10.5 mg NO_3-N/l. Powlesland and Frost (1990) calculated that a standard application rate of raw liquid sludge (4 tonnes/ha of dry solids at 3% total N) injected into the soil might be expected to increase the groundwater concentration by 0.84 mg NO_3-N/l. This value would probably be more than doubled for digested sludges due to the higher N content and N availability. For digested sludge cake an estimated increase of only 0.12 mg NO_3-N/l was anticipated, although experimental data suggest this may be an underestimation at normal application rates (12.5 tonnes/ha of dry solids, WRc 1985).

Smith et al. (1994) compared the leaching losses of N from arable and grassland soils treated with sewage sludge on the same loamy sand soil. Nitrogen leaching from grassland was 88 - 96% lower than that from arable land. Grass can use up to 400 kg N/ha before its requirements are exceeded and N starts to accumulate in the soil with a potential risk of leaching loss (Prins et al. 1988, Soon et al. 1978). Furrer and Stauffer (1986) showed that application of 700 kg N/ha in sewage sludge (which equated to approximately 400 kg N/ha of available N) did not influence the nitrate content of leachate. However, other studies (Walther 1989) show a lower "break-point" of 200 kg N/ha for grassland before leaching occurs.

If the nitrogen requirements of a crop have been exceeded, or if there is no crop cover, Smith (1996) suggests that the loss of nitrate by leaching is expected to increase linearly with increasing sludge application rate. This view is supported by the arable leaching model of Jansson et al. (1989) for sandy soils, but the model indicated that for clay soils nitrate leaching only occurs above a threshold level of nitrogen application of 120 kg N/ha.

Table 6.2 Nitrate leaching losses from a UK field study

Soil type	Crop	Sludge type	Nitrogen application rate (kg/ha)	Amount of nitrogen leached (kg/ha)/concentration in leachate (mg N/l)	Nitrate concentration in groundwater (mg N/l)
Sandy	YEAR 1	1) raw injected	September (winter or spring	(winter barley) (spring barley)	not measured
loam		sewage sludge	barley)	1) 67 /46 112 /62	
	winter or spring	2) digested injected	1) 263	2) 122 /82 160 /89	
	barley	sludge	2) 173	3) 102 /69 121 /67	
		3) digested surface-	3) 166	4) 116 /78 99 /55	
		spread	4) 644		
		4) sludge cake	November (spring barley)		
			1) 65	1) 62 /34	
			2) 720	2) 184 /102	
			3) 611	3) 74 /41	
			4) 620	4) 72 /40	
			January (spring barley)		
			1) 313	1) 56 /31	
			2) 258	2) 60 /34	
			3) 220	3) 59 /33	
			4) 462	4) 64 /36	
	YEAR 2		September (winter or spring	(winter barley) (spring barley)	
			barley)	1) 37 /18 45 /20	
	winter or spring		1) 153	2) 50 /24 77 /34	
	barley		2) 176	3) 43 /21 50 /22	
			3) 176	4) 54 /26 59 /26	
			4) 261		
			November (spring barley)		
			1) 298	1) 33 /14	
			2) 235	2) 47 /21	
			3) 255	3) 45 /20	
			4) 301	4) 43 /19	

From Shepherd (1994)

Table 6.3 Nitrate leaching losses from other field studies

Authors	Country	Soil type	Crop	Sludge type	Application rate	Leachate concentration	Groundwater concentration
Higgins 1984	USA	sandy loam	dent corn & rye grass	aerobically digested sewage sludge	3 consecutive years: 0, 22.4, 44.8 tonnes dry solids/ha	-	> 50 mg/l 1 year after sludge application at highest rate; > 30 mg/l for sludge application at lower rate.
Hinesly et al. 1974	USA	-	non-leguminous	4% solids	20.4 - 30.4 tonnes/ha	-	not excessive
Brockway and Urie 1983	USA	-	forest	municipal and papermill wastewater sludges	-	> 10 mg N/l under pine plantations receiving > 19.3 dry Mg/ha and aspen sprouts receiving > 23 dry Mg/ha anaerobically digested municipal sludge.	> 10 mg/l under plots treated with > 16 Mg/ha dry undigested paper sludge. Application rates which would not exceed 10 mg/l were thought to be: red pine-9.5 Mg/ha dry raw papermill sludge (670 kg/ha total N); red and white pine-16.5 dry Mg/ha anaerobically digested municipal sludge (990 kg/ha total N); aspen sprouts-19 dry Mg/ha anaerobically digested municipal sludge (1140 kg/ha total N)
Geertsema et al. 1994	USA	sandy loam	pine	alum sludge	0, 40, 57 dry tonnes/ha	no contamination	no contamination
Lerch et al. 1990	USA	-	winter wheat/fallow		7.5 tonnes/ha	-	maximum application rate to minimise nitrate pollution
Peterson et al. 1988	USA	silt loam	arable	-	7.5 tonnes/ha 15 tonnes/ha over 8 year period (previous application rate of 7.5)	-	10 - 21 mg/l 10 - 30 mg/l
		clay loam	prairie grass	-	5 year period		4.3 - 19 mg/l
Andersson 1982	Finland	-	-	-	170 kg N/ha 100 kg N/ha	-	major cause of nitrate pollution in groundwater no major pollution risk
Frink & Sawhney 1994	USA	sandy loam	turf (15 m x 43 m test plot)	composted sewage sludge	293 Mg (mixed with topsoil)/ha	net contribution of 5.1 mg/l from sludge over 18 months	
Grant & Olesen 1983	Denmark	sandy	spruce	anaerobically digested liquid sludge	1300 kg N (of which 1200 kg were organic N)/ha	at 50 cm depth increased after half a year to a maximum of 30-40 mg/l then decreased	maximum concentration of about 10 mg/l reached after 1.5-2 years and persisted 3-4 years. No N enrichment 6.5 years after applications

6.5 Impact of Timing of Application

In general, 30% of cake sludge is typically applied in the spring prior to sowing of crops, and the remaining 70% is applied to stubble during the period late July to October prior to drilling winter crops. This is the time when vulnerability to nitrate leaching is at its highest. Eastern England and the Midlands are located over potentially sensitive groundwater sources and have predominantly arable cropping; the potential impact of sludge application to agricultural land on nitrate leaching will be significantly larger than in western areas, which are largely grassland.

7. LAND APPLICATION OF TREATED EFFLUENT

7.1 Background

Wastewater is commonly reused in the surface water context in the UK; sewage effluent is discharged into rivers and subsequently abstracted downstream. However, discounting the spreading of agricultural slurries, groundwater recharge resulting from the disposal of wastewater is not greatly developed. It is likely that the use of partially treated wastewater to augment groundwater resources will increase in the future. Interest has been stimulated by the drought conditions experienced by the UK in recent years and perhaps by longer term concerns about the impact of possible global climatic changes on water resources. The greatest demand is likely to come in the SE of England where groundwater resources are the most heavily exploited and most susceptible to the impacts of drought. To date the most comprehensive experience of recharge with partially treated water comes from the Chalk in southern England.

Effluent disposal to land is particularly widespread over the Chalk aquifer where rivers into which effluent could be disposed are few. The total volume of effluent discharged daily to the Chalk was estimated by Baxter and Clark (1984) as 150,000 m^3 within England. A comparable amount is disposed to the Triassic Sandstone in the Midlands together with various minor aquifers.

7.2 Effluent Recharge Mechanisms

Movement of wastewater through the soil, unsaturated zone and saturated aquifer improves its quality (Foster et al. 1994). However, variations in the recharge mechanism and infiltration rate exert an important influence exert an important influence on the effectiveness of this self-purification process. In general, the slower and more intermittent the infiltration, the more effective is the self purification process.

Most of the processes resulting in pollutant elimination and attenuation in aquifers occur at much higher rates in the biologically active soil zone. If the soil is removed in the construction of lagoons and trenches, some benefits may be lost. Also, given the artificial hydraulic surcharging associated with wastewater recharge, flow rates in fissured formations may be more than an order of magnitude higher than under comparable conditions in non-fissures aquifers. The presence of fractures, fissures and other macropores is a key factor in reducing the potential for contaminant attenuation. The saturated zone is a more predictable environment, due to the lower concentration of oxygen and the dilution effects of the relatively large body of groundwater.

7.3 Methods of Recharge

A number of methods have been used in the UK for the discharge of sewage to the ground without the creation of a severe pollution problem. Case studies on the Hampshire Chalk have been reviewed by Beard and Giles (1990).

7.3.1 Land spreading

This is the cheapest and simplest option available. The effluent is allowed to run over the surface of a grass plot and soak through the soil zone into the ground. This method is apparently very effective with effluent disappearing within 20 m of discharge. It is the only method where the effluent is distributed above the soil zone and takes advantage of the soil activity. Best results are obtained from high quality effluent; primary effluent leads to the growth of fungus and deterioration of the land surface. To prevent this available carbon concentrations need to be kept below 15 mg/l which has the drawback that insufficient organic carbon is available to promote denitrification.

7.3.2 Excavated ditches

Effluent is discharged via a series of ditches excavated through the topsoil, here into the weathered chalk. This system is able to handle poor quality effluents, including primary settled effluent. The disadvantages are that a considerable land area is required, and there can be a smell problem. The infiltration performance of the ditches decreases with time as they become silted up.

7.3.3 Soakaway lagoons

A series of deep excavated lagoons can be used to dispose of secondary settled effluent. Rotation of the lagoons to allow recovery is the main method of maintenance. These have obvious disadvantages in terms of the hazard of persons falling in and the difficulties of the removal of settled solids.

7.3.4 French soakaway drains

This system has several advantages: the lack of visual obtrusiveness and odour allow construction close to the population which they serve. The disadvantages are the expense of construction and the requirement for fully treated effluent.

7.4 Behaviour of Nitrogen during Infiltration of Effluent

Nitrogen in sewage effluent may occur in several different forms - nitrate, nitrite, nitrous oxide, ammonium and ammonia and nitrogen gases - depending on the conditions. Inorganic nitrogen usually occurs in domestic wastewater as ammonium, which can then be converted to nitrite or nitrate under oxidising conditions. This nitrate can be reduced to nitrogen gas by denitrifying bacteria when conditions become anaerobic. Thus, the behaviour of nitrogen species associated with wastewater infiltration can be highly variable. For example, in schemes in coastal sand dunes in the Netherlands, almost total nitrate removal occurred following the passage of recharging wastewater through anaerobic zones, whilst little removal occurred in other areas (van Puffelen 1982).

Wastewater recharge to alluvial deposits in Phoenix, Arizona is long-established and well-described (Bouwer and Rice 1984). The scheme at Flushing Meadows dates from 1967 and that at 23rd Avenue from 1975. The groundwater is subsequently used for crop irrigation. At Flushing Meadows, total nitrogen concentrations declined from 20 mg/l to about 7 mg/l if the recharge area was managed with alternate flooding and drying-out cycles to promote denitrification. At the 23rd Avenue site, a similar reduction was observed, with a suggestion of seasonality. Only NH_4-N occasionally reached the water table at significant concentrations (Bouwer and Rice 1984). These results suggest that nitrification was complete but denitrification was partial and fluctuating. This was because the short flooding cycles favoured the active growth of aerobic microbial populations.

Experience of operating and monitoring the Phoenix sites suggests that it is possible to promote denitrification by allowing intermittent infiltration of primary effluent. With subsequent drying out of the soil profile aeration and nitrification occur. When anaerobic conditions are re-established, denitrification of this nitrate is encouraged. By careful control, this approach can reduce total nitrate concentrations in groundwater recharge to less than 5 mg N/l.

The behaviour of nitrogen in various schemes on the Hampshire Chalk also demonstrates the importance of denitrification (Tables 7.1 and 7.2) (Beard and Giles 1990). Where biologically oxidised effluent containing the majority of the nitrogen as NO_3 was used at the Whitchurch French Drain scheme, the resulting concentration of nitrogen in groundwater was similar to that in the original effluent. Where primary effluent is used as at Winchester, with a high carbon loading, it was calculated that about 50% of the total inorganic nitrogen loading is removed. At Ludgershall localised denitrification could be observed in porewater profiles from below the recharge area.

In the San Juan de Miraflores wastewater reuse scheme in Lima, Peru, both raw sewage and stabilised sewage from lagoons, is used to irrigate an area of agricultural crops, trees and parkland (Geake et al. 1986). Under the lagoons the ammonium concentrations are similar to those in the raw sewage and gradually decrease with depth, probably due to cation exchange (Figure 7.1). Under cultivated land, ammonia is negligible because of soil aeration between flood events and the promotion of oxidation to nitrate. An excess of 390 kg N/ha/a is leached by excess irrigation water, and the resulting groundwater nitrate concentrations are high.

Table 7.1 Summary of effluent recharge experiments to the Chalk aquifer in Hampshire

Method	Site	Effluent type	Volume of effluent treated (m^3/d)	N concentration in effluent (mg/l)	N concentration in groundwater at site (mg/l)
Land spreading	Ludgershall	Mixed	800	31.4	10 - 30
	Winchester	Settled	8000	27.5	3 - 11
Infiltration ditches	Whitchurch	Secondary settled	700	18.7	15 - 20
French drains	Whitchurch	Biologically oxidised	900	20	20

From Beard and Giles (1990)

Table 7.2 Percentage nitrogen removal at Hampshire wastewater recharge sites

Recharge site	NH_4-N	NO_3-N	NO_2-N
Winchester	90	90	94
Whitchurch (before 1981)	16	91	99
Whitchurch(after 1981)	30	5	78
Alresford French drains	83	20	94
Alresford soakaway	99	25	93
Ludgershall	99	4	99
Caddington	75	45	-

After Beard and Giles (1990)

7.5 Impact on Groundwater

The impact of the high hydraulic loading at the Winchester site can be seen in the penetration of nitrate to depth in the aquifer (Beard and Giles 1990). Contamination extends as far as 85 m below the water table. In contrast at Ludgershall, contamination was restricted to the zone of water table fluctuation (9 - 20 m). Measurements of chloride were useful in determining the extent of groundwater contamination with wastewater. The conservative nature of the chloride ion means that its concentration is only reduced by dilution. Chloride was shown to return to background concentrations within 3 km downgradient at all sites in this review. At the site at Caddington, Hampshire, as described by Baxter and Clark (1984), saturated zone nitrate concentrations approach or exceed the effluent concentration decreasing to background within 2 - 3 km of the site (Figure 7.2).

At an agricultural wastewater reuse scheme in Leon, Mexico, all water within the shallow aquifer was shown to be contaminated with nitrate and high concentrations of chloride were also observed (BGS et al. 1995). Concentrations exceed the WHO limit for potable supply, but some groundwater is presently used for agricultural irrigation.

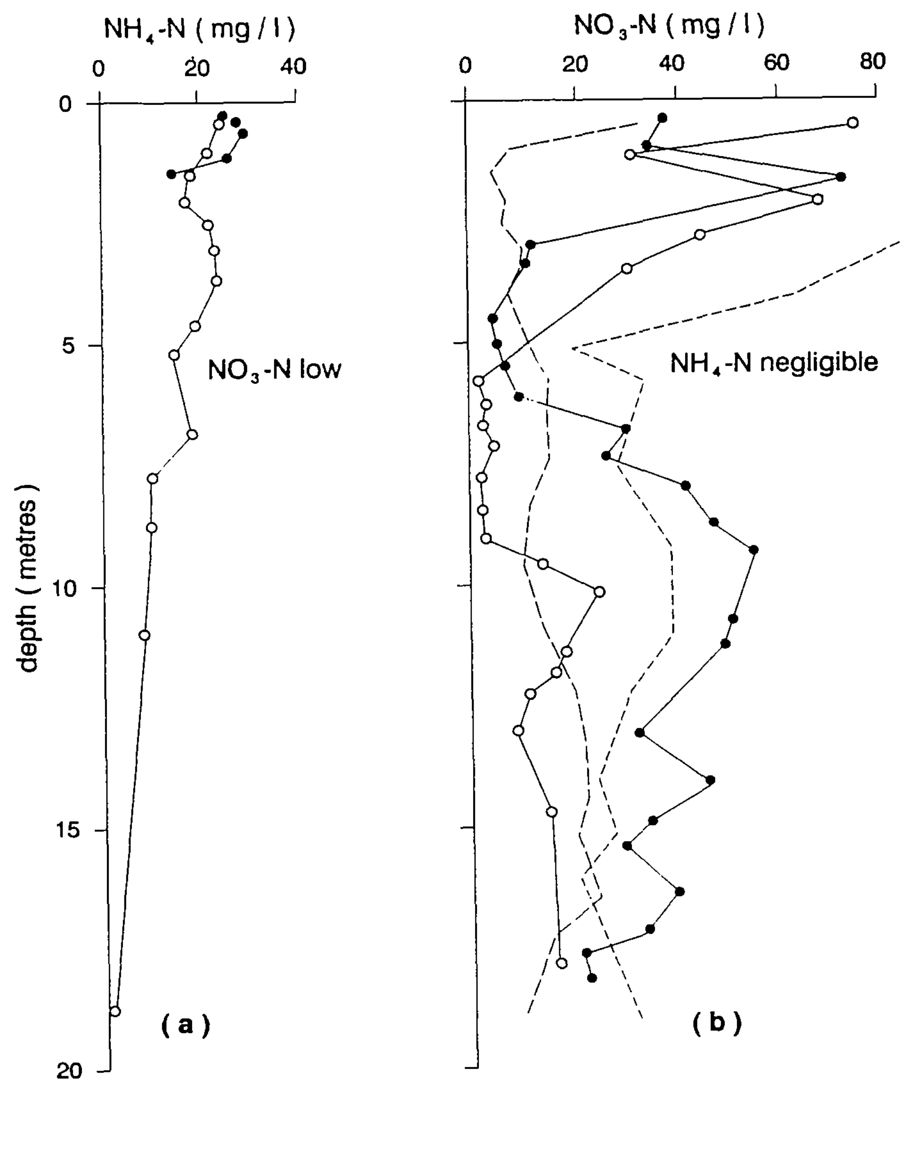

Figure 7.1 **Nitrogen profiles in the unsaturated zone at Lima, Peru. a) beneath wastewater lagoons, b) beneath cultivated land (after BGS et al. 1995)**

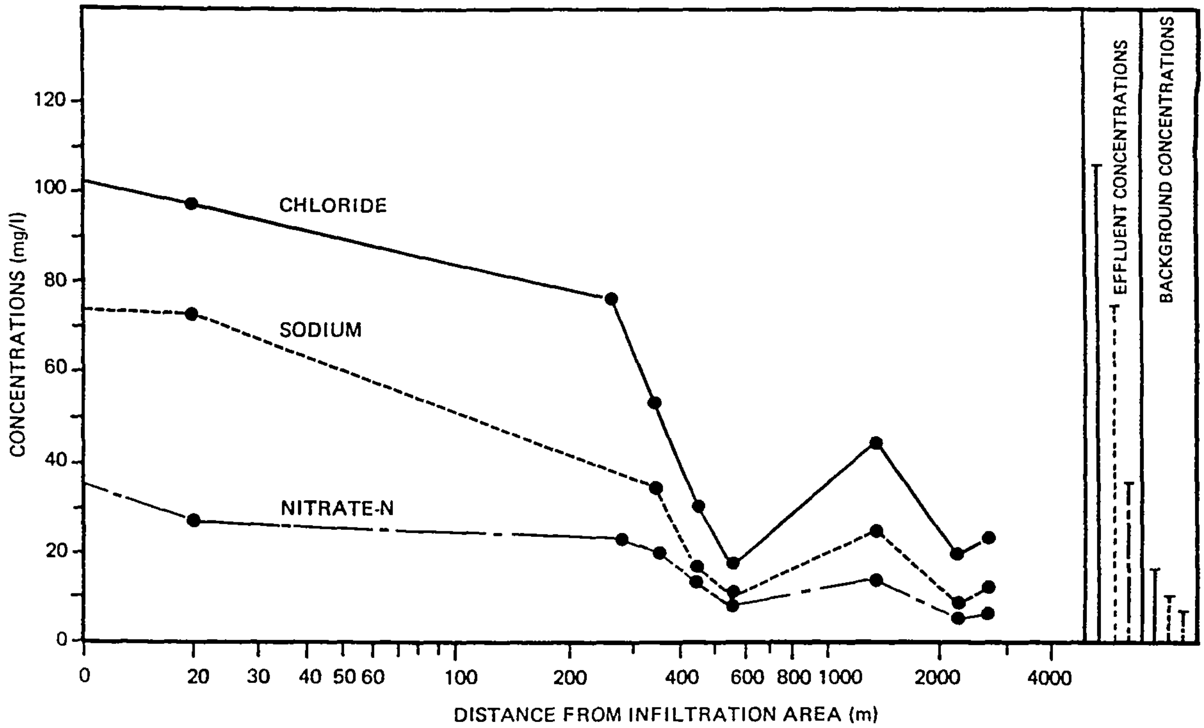

Figure 7.2 Water quality profile down groundwater gradient from area of effluent recharge at Caddington, Hampshire (from Baxter and Clark 1984)

8. INTENSIVE LIVESTOCK REARING

8.1 Background

Nutrient contamination of surface and groundwater associated with livestock rearing has become more common as the industry has become more intensive. Between 1987 and 1989, most serious cases of agricultural pollution to surface water came from leakages of slurry, silage effluent and dirty water (MAFF 1991). The storage and disposal of slurry, dirty water, silage effluent and solid manure are covered by the Code of Good Agricultural Practice for the Protection of Water (MAFF 1991)

Bowmer and Laut (1992) considered the potential sources of pollution for intensive rural industries in Australia to be beef cattle feedlots, piggeries, dairy farms together with abattoirs, tanneries, meat and poultry processing plants. This chapter also reviews the potential impact of silage clamps and slurry stores.

8.2 Feedlots and Barnyards

Keeney (1986) reviewed the information on the potential for nitrate leaching beneath feedlots and concluded that feedlots and barnyards do not constitute a major nitrate source to regional groundwater. The surface of an active feedlot is high in organic material which is mixed with soil by the action of the cattle. Beneath this zone, is the mineral soil surface often packed to a high bulk density. This horizon may be nearly impermeable to water and oxygen so little nitrate is formed or leached whilst the feedlot is in use. However, when feedlots are abandoned or completely cleaned of manure nitrate can be formed and leached and this has been observed (Ellis et al. 1975). Saint-Fort et al. (1991) showed that the highest concentrations of nitrogen in subsurface soils in a Nebraska catchment were found beneath feedlots, where concentrations of up to 120 mg NO_3-N/l were observed. However these fell to less than 5 mg NO_3-N/l below 3 m. When the actual relative area is taken into account, the mass contribution is small relative to cropland (Table 8.1).

Table 8.1 Potential water pollution from feedlots

Stock type	Waste volume (m^3/head/year)	Nitrogen (kg/head/year)
Beef cattle	20.2	80.3
Pigs	1.6	8.4
Battery chickens	0.04	0.51
Sheep	1.8	8.4
Turkeys	0.04	0.51
Ducks	0.04	0.51

From Gleick 1993

8.3 Farmyards

Aldwell et al. (1983) reported that waste from farmyards and other areas of livestock concentration was the most common and widespread source of groundwater pollution in Ireland. The runoff from farm buildings and yards has a high content of organic compounds and suspended solids. *It is* estimated that up to 1000 m^3/farm/year of wastewater is produced, which soaks away beneath the farm yard area. The majority of cases of pollution of surface waters by farm wastes in the UK are caused by discharges of effluents from around yards and buildings (MAFF 1984). In order to control these problems it is recommended that:

- The volume of water allowed to enter animal slurries should be minimised unless required for handling purposes. Storage facilities must be designed to cope with the volume of waste produced under occasional extremes of weather. Wash waters from dairies, collecting yards and livestock buildings, and liquid draining from middens and slurry stores must also be provided for.

- Leachates from feedstuffs such as brewers grains and from vegetable wastes is highly polluting and needs to be collected.

- The consent to discharge vegetable washing waters usually requires some form of pre-treatment such as settlement and particulate removal.

- Water from roofs and clean areas of concrete should be collected separately and may be discharged to water courses or drains.

- Dirty water is defined as slurry and regulated as such.

8.4 Slurry Storage

8.4.1 Regulation

The Control of Pollution (Silage, Slurry and Agricultural Fuel Oil) Regulations 1990 lays down requirements for new, extended or substantially reconstructed stores and reception pits. The main requirements include:

1. No part of the store should be sited within 10 m of a watercourse.

2. Floors should be impervious.

3. Walls and floors should be capable of withstanding specific loads.

4. The store should have an anticipated 20 year life expectancy.

5. The store should be capable of containing at least four months effluent.

8.4.2 Evidence of pollution

There is evidence that in 1990 many dairy farms only had sufficient storage for one month of slurry production and many pig farms for two (Baldock and Bennett 1991). Surveys in the SW of the UK in the mid 1980s indicated that up to one quarter of intensive dairy farms visited were causing pollution at the time of the visit and that a further quarter were engaged in practices which created a pollution risk.

Storage facilities constructed before the introduction of the regulations are not covered unless they are causing obvious pollution and many farms still use lagoons for the storage of slurry. It is assumed that there is an initial flush of nitrogen from a lagoon as it begins operation but that as it starts to seal, the leachate improves in quality. Organic nitrogen is removed by filtration in the mat that develops. Anaerobic lagoons do not normally contain oxidised nitrogen. Korom and Jeppson (1994) studied nitrate contamination from two lagoons constructed in coarse alluvial deposits in Utah, and used to store slurry from dairy cattle. They found that nitrogen concentrations in leachate from both lagoons substantially exceeded 11.4 mg/l even after several years of operation. Similar results were obtained by Tellez et al. (1992) who found concentrations of nitrogen up to 40 mg/l in groundwater downgradient of dairy shed waste ponds.

Gooddy et al. (1994) studied the impact of dairy slurry storage in an unlined chalk pit at the ADAS agricultural station at Bridgets farm in Hampshire. They found extremely high concentrations of both nitrate and ammonia (up to 800 mgN/l) in porewaters of the unsaturated zone. The fissured nature of the Chalk had allowed the penetration of slurry to depths in excess of 30 m in the 14 years of operation of the pit. The deep water table at this site (>50 m) meant that groundwater was not yet seriously affected but elevated concentrations of many ions, including ammonium were seen in a nearby observation borehole.

8.5 Silage

8.5.1 Regulations

New or substantially reconstructed silos must now conform to the Control of Pollution (Silage, Slurry and Agricultural Fuel Oil) Regulations 1990. The main requirements are:

1. The silo base should be impermeable and be provided with perimeter channels for effluent collection.

2. Where walls are provided, the silo base should extend beyond the walls to provide channels for effluent collection.

3. Collection channels must lead to an effluent tank which is resistant to acid attack. It should have a minimum capacity of 3 m^3 per 150 m^3 of silo capacity up to 1500 m^3.

4. No part of the silo, effluent tank or channels should be within 10 m of a water course.

Neither of the two above categories include existing storage facilities which therefore may have a greater potential to pollute water. It is clear that these regulations are designed to minimise surface water problems, but that groundwater will also be protected.

Silage was the most common source of pollution on UK farms in 1985 (MAFF 1985) with a number of prosecutions occurring each year. The amount of liquor produced during silage making is related to the dry matter content of the original material, and can vary from almost zero for material with over 25% dry matter content to about 400 l/tonne for 10 - 15% dry matter. This effluent is high in suspended solids, N and biological oxygen demand and in addition is highly acidic (Aldwell et al. 1983).

8.6 Piggeries

There three major approaches to the production of pigs: open pasture, open feedlots and roofed confinement facilities (Schaffer and VanderMeulen 1987). Waste management at open-lot facilities includes the need to remove manure from the open lot and housing units. The solid manure can be mechanically scraped off and stockpiled for field spreading. Runoff control is a critical part of semi-confinement management and facilities need to include a settling basin, plus a holding pond for storage.

The production of pigs in outdoor units is gaining in popularity in the UK and is often concentrated on free-draining soils over important aquifers (Worthington and Danks 1992). Increases in the stocking rates (up to 25 sows/ha) means that the natural rooting and wallowing activities of pigs lead to considerable damage to vegetation and soil structure, and consequently to extensive areas of bare ground for much of the year. By estimating the N budget for an outdoor pig unit, Worthington and Danks (1992) calculated that there was significant potential for leaching of nitrate, with some 420 kg N/ha remaining available in the soil.

8.7 Livestock Disposal

8.7.1 Regulations

Disposal methods for animal carcasses on the farm include burial, incineration or burning in the open air. Under Part II of the Environmental Protection Act (1990) it is an offence to apply any waste to land which is likely to damage the environment. Carcasses may be disposed into burial pits conforming to the following regulations (MAFF 1991). The site must be:

1. 250 m away from any water abstraction point used for human consumption or dairying

2. 30 m away from any surface water course and 10 m away from any drain.

3. Having 1 m of subsoil above and below.

4. Free of standing water

8.7.2 Research

Groundwater quality was monitored for nitrogen compounds, chloride and coliforms around six disposal pits used for dead battery chickens located on sandy soils by Ritter and Chirnside (1995). Elevated concentrations of ammonia in the groundwater, to a maximum of 366 mg NO_3-N/l were detected at three of the sites. The amount of nitrogen leached was equivalent to a single septic disposal system.

8.8 Extent of Waste Management Problems

It was estimated that the total production of livestock wastes in England and Wales amounts to over 200 million tons annually and these are the largest source of agricultural surface water pollution. Reviews of waste disposal problems tend to concentrate on the very high risk to surface water, but waste production on this scale must also pose a threat to groundwater.

The results of a study by the Severn Trent region of the EA of dairy farms in Shropshire showed that many had unsatisfactory facilities for the storage of large volumes of waste, especially slurry (and other elements of waste handling) (Table 8.2). A breakdown of farm pollution incidents for the UK in 1985 - 9 are discussed by Baldock and Bennett (1991). Pollution associated with cattle farms accounted for up to 80% of recorded incidents, with pig farms adding a further 10%. It is not known how many farms were engaging in practices with represented a potential water risk, but it was thought to exceed considerably the 4000 farms involved in recorded incidents each year.

Table 8.2 Survey of pollution risks in dairy farms in the Midlands, 1989/90

Category of risk	No of farms surveyed	% Doubtful or unsatisfactory
Drainage	162	16.7
Solid waste	934	19.1
Silage	891	35.9
Dairy	644	37.6
Slurry	811	39.5
Contaminated yard	724	41.7

From Baldock and Bennett 1991

9. LANDFILLS

9.1 UK Waste Disposal Policy

There are thousands of landfill sites in the UK. Many are old and disused and fall into the category of contaminated land. The pollution risk was not taken into account in choosing the sites and little effort was made to prevent pollution or to monitor the groundwater around them.

Since 1976, landfilling in the UK has been controlled by a system of site licensing by waste disposal authorities. The variation in geology and annual rainfall over the UK has meant that there is no typical landfill site or method of construction (Robinson and Gronow 1992). The legislation to control the landfilling of wastes has now altered, with the implementation of EC Directive 80/68/EEC (CEC 1980). This limits the development of landfills based on the "dilute and disperse" principle, and landfill design has moved towards containment of leachate. However modern landfills have to be large to be economically viable and there are no legal requirements governing the type of lining that must be used or the permeability of the underlying clay material, although good technical guidance is now available.

Following the passing of the Environmental Protection Act in 1990, new Waste Management regulations came into force in May 1994. These replace the relevant sections of the 1974 Control of Pollution Act and represent a radical change in waste regulation. The new provisions also implement the requirements of EC Directive 75/442 (CEC 1975) on Waste as amended by Directive 91/156 (CEC 1991). They also seek to implement provisions of the Groundwater directive by requiring applicants to include a hydrogeological study and risk assessment where a site might impact on local groundwater. Waste Regulatory Authorities are also required to review all licences which have groundwater implications.

Although nitrate pollution from recently constructed landfills is less likely, the production of highly polluting leachate is an inevitable consequence of the disposal of household wastes in the climate of the UK. Whilst good practice will reduce the quantity of leachate produced, leachate management must be planned at all sites. Extensive monitoring of groundwater quality around landfills is performed by the operators, by the Waste Regulatory Authorities and by the EA. The Groundwater Protection Policy directs potentially polluting activities, such as landfill, away from areas of greatest vulnerability and the siting of new sites is closely scrutinised.

9.2 Nitrogen in Landfill Leachate

The internal biochemical decomposition processes that take place within a landfill containing putrescible wastes play a crucial role in determining potential adverse impacts both during and after the active life of a landfill. Particularly important is the change from early acetogenic conditions where high organic strength leachates are generated, to later methanogenic stages of decomposition, where these organic compounds are actively converted to landfill gas (mainly carbon dioxide and methane).

Ammoniacal nitrogen is released as wastes undergo acetogenic decomposition, and concentrations in excess of 1000 mg/l are often measured (Robinson 1989). Once released into the anaerobic environment of a landfill site there is no significant removal pathway other than ammonia in leachate. However, leachate which migrates away from a landfill site is likely to encounter aerobic conditions in the aquifer, which will enable nitrification of ammonium to nitrate. Prior to nitrification, ammonium may be attenuated by adsorption onto clay in the aquifer. Thus the prediction of nitrate concentration in groundwater from a leachate plume is a difficult process.

9.3 Impact on Groundwater

Bjerg et al. (1995) studied concentrations of ammonium and nitrate in a leachate plume from a landfill in Denmark. The landfill lies on a shallow sandy aquifer, is unlined and contains about 500 000 m^3 of waste. The leachate plume is recognizable for about 200 - 250 m down dip from the landfill; the ammonium concentration is 116 mg/l close to the landfill and decreases with distance. Nitrate concentrations are low close to the landfill, but an envelope of high nitrate water surrounds the plume. However, the nitrate does not greatly exceed the background concentration (0.5 - 5 mg/l) of nitrate from agricultural sources.

Kimmel and Braids (1980) also studied ammonium and nitrate in landfill leachate on Long Island, New York. Ammonium concentrations close to the landfill were 46 mg/l, with low nitrate. Nitrate concentrations increased downgradient to about 40% of the total nitrogen near the toe of the plume. Within the plumes, nitrate concentrations did not exceed the recommended limit of 10 mg/l NO_3-N.

A detailed study of landfill leachate composition has been carried out by Aspinwall and Company (Robinson 1995) on behalf of the Department of the Environment. Landfill sites were divided into the following categories, which were thought to be broadly representative of typical landfill types in the UK:

1. Large landfills, high waste input, relatively dry
2. Large landfills, high waste input, deep, wet and "bioreactive"
3. Large, deep landfills, wet and "cold"
4. Small landfills, operated with limited water ingress
5. Small landfills, operated with some control of water ingress
6. Small landfills, relatively wet
7. Large, flat and shallow landfills
8. Landfills with a high percentage of baled wastes
9. Landfills with a high percentage of pulverised wastes
10. Valley landfills with groundwater ingress
11. Old landfills, poorly restored

Ammoniacal nitrogen is thought to be one of the greatest long-term concerns in landfill leachate with high concentrations often measured at the larger landfill sites, which remain reasonably stable until the wastes are fully decayed, showing no significant change as landfill conditions develop from acetogenic to methanogenic. Most large landfills now being developed in the UK fall into the first category. Ammoniacal nitrogen concentrations are of the order of 2000 mg/l; however, containment of leachate should prevent this from contaminating groundwater, although all landfills will leak eventually.

The environmental protection measures required are making smaller landfills less economically viable; however, a high proportion of landfills which have been operated, and continue to receive domestic wastes, can be classed as small. Although becoming less common, small landfills are likely to continue in the UK, particularly in rural areas. Only a few of the small landfills operated since the early 1980's can be considered to have been operated to high standards, with leachate controlled to prevent unacceptable discharges. A much higher proportion has been operated with limited or no control. As most of the wettest areas of the British Isles are on the western coast and have largely rural populations, small landfills are likely to be common and are likely to receive high levels of water ingress, and to have the potential to generate large volumes of leachate. High dilution of leachate may render it acceptable for discharge; however, many incidents of pollution of surface watercourses, often on a minor but continuous scale, occur from landfills of this type. Groundwater pollution is less common, as these western coastal areas rarely overlie important aquifers.

The greatest cause of concern about leachate pollution is from old, poorly restored landfills. Several thousand of these exist in the UK; the locations of many of them are not even known accurately. Without extensive investigation, the risks which they pose to the environment cannot confidently be assessed. Examples of old landfills which have contaminated groundwater include Foxhall, near Ipswich, which has received remediation work by Aspinwall and Company. This first received domestic waste in 1963; monitoring boreholes showed a progressive decrease in local groundwater quality. Seepage of leachate also threatened to affect the quality of a nearby watercourse; it was predicted that landfill leachate would raise ammonium concentrations in the river from a background of 0.1 mg/l NH_4-N to 4.5 mg/l NH_4 -N. Other pollution incidents are continuing to emerge. However, given the lack of detail that exists on historic landfill sites, nitrate pollution from them will be difficult to predict.

10. AIRFIELD DE-ICING WITH UREA

10.1 Usage

Urea has traditionally been used as a de-icer on military and civil airfields. However, de-icing practices are moving towards less polluting de-icers; glycol or the more expensive Clearway 1, based on potassium acetate, are now used in almost all civil airports in England and Wales (O'Connor and Douglas 1993). RAF airfields have been slower to change, and urea or urea-based products are still widely used. There has been concern that RAF airfields which lie over groundwater containing high concentrations of nitrate may be contributing to nitrate pollution. Smith-Carington et al. (1983) considered that RAF Cranwell and Waddington on the Lincolnshire Limestone could be a locally significant source of additional nitrate pollution. RAF Marham, on the Chalk in north-west Norfolk may also be important. As a result, the RAF are considering use of low-nitrate de-icing chemicals in and around NVZs.

10.2 Nitrate Leaching

The fate of nitrogen in urea after it has been applied to runways is uncertain. Some may be lost by ammonia volatilisation from the hard surface. The rest may be washed off the runway by rain or melting snow, onto land where it breaks down into ammonia, which can volatilise, be bound to the soil, or be converted into nitrate or organic nitrogen. As de-icing compounds are used during cold weather the rate of transformation of urea to nitrate will be slower than the transformation of fertilizer urea which is generally applied from spring to autumn.

Quantifying the contribution made by airfield urea to groundwater nitrate is very difficult. None of the following are known: the amount of urea which is washed off the runway onto land; the rate of transformation; the extent to which ammonia is converted to nitrate or lost by volatilisation or immobilisation. If a "worst case" assumption is made that all the applied urea is converted to nitrate, the amount of urea applied over recent winters is equivalent to losses from the following areas of arable land:

RAF Marham	up to140 ha
RAF Cranwell (and Barkston Heath)	up to 76 ha
RAF Waddington	up to 296 ha

These areas are less than the areas of the airfields, indicating that the contribution of nitrate from de-icers is likely to be less significant than that from agriculture. It is also likely that the actual contribution is likely to be much less than that calculated for the worst case situation.

11. RIVER AQUIFER INTERACTION

11.1 Water Movement

Where rivers run over aquifer outcrops there is potential for river-groundwater interaction, for rivers to either lose water to the aquifer or to gain water. Along a stretch of river, or at different times of year on the same reach of river, both processes may operate. The movement of water is governed by the relative heads of water in the river and the aquifer and the intervening bank and river bed sediments. The movement of river water into an aquifer occurs by two main processes (Younger 1987):

- Bank storage: this occurs where the river stage is above, but in contact with the aquifer and water is stored in the aquifer around the river, with a head gradient away from the river. This infiltration process is then reversible if the river stage subsequently declines.

- Recharge to the aquifer occurs if the river is perched over the aquifer and there is no possibility of return of water to the river.

In addition wells or boreholes drawing groundwater from close to a river can cause local induced infiltration of river water into an aquifer. This is likely to be the most important source of river water to boreholes.

It has been demonstrated (Casey 1969, Pinder and Jones 1969, Sklash and Farvolden 1979) that groundwater makes a significant contribution to storm runoff, comprising up to around 50% of peak discharge. After studying numerous runoff events for a variety of basins in Scandinavia, Sklash and Farvolden (1979) concluded that "for all except the most intense rainstorms and the most prolific melting days, groundwater dominates the runoff hydrographs in the study basins". So it is thought likely that streams and rivers that are generally gaining will remain so during short periods of high discharge.

11.2 Techniques for Analysing Interaction

Techniques for the analysis of river-aquifer interactions on a catchment scale include:

- Flow from the aquifer to the river
  - methods for stream flow hydrograph separation
  - duration curve analysis

- Flow between the aquifer and the river
  - water budget calculations
  - observations of low-flow stream discharge quantity and quality
  - modelling

Techniques for short-term, local river-aquifer interaction analysis include:

- Flow from the river to the aquifer
  - induced filtration studies
  - modelling

The movement of water is dependent on the head in the river (taken as the upper surface of water in the river), and the groundwater head. There are a number of ways of representing the groundwater head interacting with the river. Rushton and Tomlinson (1978) take the average head vertically below the river. This assumes that flow is mainly horizontal and not vertical. It is apparent that different aquifers have different river-aquifer interaction patterns. Models frequently represent the leakage between aquifer and river as a linear relationship dependent on the head difference and the intervening permeability. However the relation of head difference to volume of leakage may be nonlinear, with greatly increasing leakage for only a small increase in head difference (Rushton and Tomlinson 1978).

11.3 Representation of River-aquifer Interactions

The methods for calculating the volume of pumped water induced from rivers were summarised by Younger (1987), and can be used along with chemical tracing methods to estimate river infiltration. Recently river infiltration has been studied using modelling techniques (Younger 1987). There are many models of river-aquifer interaction, including many analytical models for the determination of induced infiltration. However, only numerical models are capable of dealing with complex geometries and simultaneous solution of both surface and groundwater flow. One of the main difficulties in coupling surface and subsurface flow is the differing time scales of transient process in the two systems. Numerical river-aquifer interaction models which only consider transient groundwater conditions generally use an "external coupling" technique, where baseflow discharge is calculated and then used as the basis for a simple water balance calculation. Where transient conditions in the aquifer and the river are simulated it is usual to simultaneously solve the two sets of flow equations so that the output of both sets of equations satisfies an internal boundary condition. This is termed "internal coupling".

The representation of rivers in models requires some assumptions about the river and its relation to the aquifer. These are summarised by Recking (1992). Basic modelling of rivers assumes that the river fully penetrates the aquifer. This is rarely true (with the possible exception perhaps of river alluvial aquifers) as it means that the river effectively splits the aquifer into two. Another common assumption is that the river is in perfect hydraulic continuity with the aquifer. This is only valid when the river flows directly over outcrop with no significant river bed deposits, and is likely to vary along the river length. More sophisticated models include some form of resistance to flow at the river-aquifer boundary. The actual permeability of the river bed sediments is likely to depend on the grain size of the sediment, which will indicate a minimum permeability. Any macropores within the sediment will tend to increase the permeability. Younger (1990) found that the laboratory hydraulic conductivity of Thames river bed silt was 0.002 - 0.0024 m/d, but obtained bulk values from model calibration of 0.2 m/d. Examples of previous work on defining river-aquifer interactions are given in Tables 11.1 to 11.3.

Table 11.1 Examples of river-aquifer interaction in Chalk and Great Oolite by region

Region	Aquifer	Type	Example	References
Southern	Chalk	Baseflow fed rivers losing water as groundwater levels decline.	Upper reaches of River Dour lose water in spring (and then go dry) Lower reaches only lose water in late summer (when gwl are lowest)	Cross et al. 1995
Southern	Chalk	Baseflow fed rivers, local losses to aquifer near pumped borehole.	River Gripping gains on average 10-18 Ml/d (monthly averages). River only lost water in Nov. 1973 (0.2 Ml/d).	Jackson and Rushton 1987
Thames	Chalk	Baseflow fed rivers	Bournes (Lambourn and Winterbourne) mainly gain groundwater	Oakes and Pontin 1976
Thames	Chalk	Baseflow fed rivers, local losses and gains	Pumped BH near the Thames at Gatehampton may induce river-aquifer inflow at times of high flow. Amount depends on pumping rate.	Robinson and Banks 1987, Charalambous et al. 1995
Thames	Chalk	River losses to aquifer induced by pumping	River loses to aquifer in vicinity of Taplow BH	Edmunds et al. 1976
Thames	Chalk	Groundwater fed rivers in Berkshire downs and Kennet valley	All rivers generally gain, most flow in river Winterbourne, Kennet, Pang, Lambourn, Og, Albourne and Dun is baseflow.	Rushton et al. 1989
Thames	Great Oolite	River groundwater fed and gains especially in upper reaches, some local losses to aquifer.	Upper Thames gains from the Great Oolite, though some water in Upper Thames catchment is lost to Inferior Oolite. River Churn gains in upper reaches, but loses in places due to abstraction, in dry summers over 10 Ml/d may be lost from the river lower in the catchment Ampney Brook gains in winter but is dry in summer. River Coln generally gains from both Great and Inferior Oolite. River Leach: in summer gains from Inferior Oolite and local loses to Great Oolite.	Rushton et al. 1992

Table 11.2 Examples of river-aquifer interaction in the Triassic Sandstone by region

Region	Area and type	Example	References
Midland	Nottingham area, rivers both gain and lose to the aquifer.	PWS BH Everton, Elkesley and Budby near rivers experienced quality problems. Spot gauging along rivers indicates river loses to aquifer near pumped BH, though loses are rarely in excess of 1 - 2 Ml/d/km River coefficient typically 1000 m^2/d. Water balances of whole rivers indicate some losses to the aquifer and some gains[2]. Transient modelling indicates seasonal variation in volume of aquifer discharge to rivers.	Bishop and Rushton 1993
Midland and NE	Doncaster area	River Torne loses to the Sherwood Sandstone in its lower reaches between the Aukley Gauging station and Torne Bridge, at a rate of 1-1.6 Ml/d/km. Aquifer-drainage ditch interaction is also thought to occur. Through time, both the River Torne and the drainage ditches have changed from gaining from the aquifer to recharging the aquifer, especially in dry years such as 1976 and 1989-92.	Brown and Rushton 1993
Midland	Midlands Hatton Catchment	Meece Brook loses to the aquifer near pumping stations. Increase in nitrate (to over EEC limit) under existing land use into next century have been forecast. Meece Brook assumed to dilute groundwater nitrate [2].	Hatton Catchment nitrate study 1988 MAFF, STW, DoE
Southwest	River Otter may lose when aquifer pumped near river	Model of Otter Catchment allows flow to and/or from river Otter.	MRM Partnership, 1989
Northwest	West Cumbria	Measured bed losses are incurred due to groundwater abstraction close to River Calder	Internal NRA Hydrogeological Reports 1982/3
Northwest	Fylde, Lancashire	Bed losses to aquifer via permeable layers within glacial drift occurring at certain conditions have been modelled for Wyre catchment	EA Water Resources Study (1996)
Northwest	North Cumbria	Measurable losses to baseflow in small rivers flowing on drift arising from introduction of new source in previously untapped aquifer	Internal EA investigations, Confidential

[1] Bishop and Rushton (1993) describe the aquifer leakage at a nodal point (which represents 1 km length of channel) as dependant on the river coefficient, which is typically 100 m^2/d. So that a head difference of 0.5 m with the river below the groundwater level would lead to a flow of 500 m^3/d out of the aquifer, this would increase to 1000 m^3/d if the head difference is increased to 1 m.

[2] The nitrate model indicates that Meece Brook acts as an additional source of lower nitrate water (lower than groundwater), which moderates the rise in pumped nitrate levels. In this catchment the moving of the BH to areas of the catchment with lower leaching would not solve the problem.

Table 11.3 Examples of rivers with both gaining and losing sections

River Name	River sections across the aquifer outcrop area			River bed coefficient ($m^2/d/km$)
	Western section	Central section	Eastern section	
Ryton	Aquifer gains	Aquifer gains then loses to the river	Aquifer loses to the river	925
Poulter	Aquifer loses to the river	Aquifer loses to the river	Aquifer gains from the river	750 - 925
Meden	Aquifer loses to the river	Aquifer gains then loses to the river	Aquifer gains from the river	750 - 925
Maun	Aquifer gains then loses to the river	Aquifer gains from the river	Aquifer gains from the river	500 - 925
Idle	No long term significant gains or loses, outflow from central part of aquifer.			100 - 2000

After Bishop and Rushton 1993

11.4 River Chemistry

Generally groundwater is more highly mineralised than direct runoff (Younger 1987). Exceptions to this include tidal reaches which have increased salinity, and areas where there is discharge directly into rivers from industry, from sewage treatment works (STW) or from other sources of increased salinity. Anglian Region of the EA have made preliminary estimates of the nitrate loading from sewage treatment effluent in the Moulton Nitrate Vulnerable Zone (NVZ) to compare it with the likely loading from agriculture. Three small and one larger STW discharge in the NVZ. The estimate of nitrate loadings from these sewage treatment works used a value of 30 mg/l as NO_3 for the effluent concentration at outfall and the consented discharge. The total load entering the rivers within the NVZ from STW effluent was therefore some 30 kg N/d. The NVZ includes some 15,000 ha under cultivation, from which some 25 kg N/ha is likely to be leached from clayey soils and an average of 40 kg N/ha from more sandy soils. The total input to the catchment from agricultural sources is therefore, some 1000 to 1500 kg N/d, and even allowing for uncertainties in these figures the contribution from sewage treatment effluent is only of the order of 1-2%.

11.4.1 The role of river bank deposits

As water passes from a river into an aquifer bank filtration occurs. Concentrations of various solutes and suspended solids are reduced by the filtration effects of the bank material (Younger 1987). In wide deep lowland rivers such as the Thames, stream bed sediments are usually dominated by fine-grained minerals (especially clays) and organic matter, which have a low hydraulic conductivity and a high rate of biological activity, both reducing and oxidising conditions may be present (Younger et al. 1993).

Jacobs et al. (1988) describe the chemical changes that occur along the river-groundwater infiltration flow path for the Glatt river in Switzerland, downstream of several biological-mechanical sewage treatment plants, which contribute 15 - 20% of the 8 m^3/s discharge. In this study, water was assumed to flow into the aquifer with an average linear velocity of 2 - 4 *m/d. The* behaviour of nitrate varied. This may result from the balance between nitrification and aerobic organic matter degradation increasing nitrate, and denitrification which decreases nitrate concentrations. Variations in mixing and river chemistry are considered a more likely cause. NH_4^+ concentrations were always below detection limit in groundwater samples and it is assumed that all the ammonium in the river water was consumed by nitrification in early stages of recharge. River chemistry showed marked diurnal variations in nitrate and ammonium concentrations. The study of the Glatt river concludes that: "Organic matter degradation is the major process controlling concentration changes in the principle inorganic constituents during the early stages of recharge. These changes can be assessed quantitatively using mass balance calculations that include redox reactions (oxygen respiration, nitrification, de-nitrification), weathering reactions (carbonate precipitation/dissolution and quartz dissolution) and CO_2 gas exchange." Most of these changes are thought to occur shortly after infiltration (within the first day after infiltration) (Jacobs et al. 1988).

Tank experiments using river water pumped over river bed sediments from the Afon Teifi, Wales, demonstrated a rapid decrease in nitrate-N within fine sediment over a period of 100 hours, at both initially high ($\leq$ 12 mg NO_3-N/l) and initially low ($\leq$ 2.5 mg NO_3-N/l) concentrations of nitrate to final values of $\leq$ 2 mg/l. This corresponded to a removal rate of 45-200 mg NO_3-N/m^2/d. There was a corresponding increase in ammoniacal-N in these fine sediments. At low initial nitrate concentrations coarser gravels and cobbles produced an increase in nitrate equivalent to 10 mg NO_3-N/m^2/d, whilst intermediate gravels showed an intermediate rate of 15 mg NO_3-N/m^2/d. At high initial nitrate concentrations, nitrate removal was seen in the coarser sediments. Nitrate removal is associated with fine sediments and associated reducing conditions and high organic carbon content which provides a substrate for denitrifying bacteria (Wyer and Kay 1989). Laboratory studies of nitrate removal rates by bank sediments are summarised in Table 11.4.

11.4.2 Chemical tracers of river water

River water has been traced into aquifers with varying degrees of success, using a variety of methods. However the chemical reactions occurring as river water infiltrates into an aquifer must be considered when attempting to trace river water chemically. These reactions will modify the composition of the recharge water. Studies of the Lot river in France have used chloride as a conservative tracer to monitor changes in concentration of other ions (Bourg and Bertin 1993). Case studies are summarised in Table 11.5.

11.5 Boreholes near Rivers

There are a number of public supply sources using boreholes near rivers which obtain some part of their water from the river as well as from the aquifer. These borehole may be very high yielding and important for public supply. Examples of these are given in Tables 11.6 and 11.7.

Table 11.4 Laboratory studies of nitrate removal rates from incubations of stream sediments and water.

Reference	Study area	Removal rate (mg NO_3-N m^2/d)	Temperature ^0C	Initial concentration (mg N/l)	Comments
Van Kessel 1977	Netherlands	374	19	6.5	Average of intact cores
Chatarpaul et al. 1980	Ontario	90	15	9.1	With Turbificid worms
		50	15	9.1	without Turbificid worms
Wyer and Hill 1984	Ontario	11 - 171	21	5	Wide range of sediment types
Wyer and Kay 1989	Wales	15 - 49	24	2	Stream water used as diluent
		67 - 241	24	11	

After Wyer and Kay 1989

Table 11.5. Case studies of chemical river aquifer interaction

Reference	Study area	River aquifer interchange	NO_3 - N conc of river	Model	Comments
UK					
Wyer and Kay 1989	Afon Teifi Wales	-	3.5 mg/l	-	-
Europe					
Bourg and Bertin 1993	Lot river France	Infiltration of river water into alluvial aquifer	-	Use chloride as a tracer (lower in river water).	Nitrate concentrations reduced in river bank area (2.5 x 10^{-5} mol/l nitrate consumed).
Meinardi and Grakist 1985	Netherlands	BH pumping induced bank filtration	-	-	Wells 1 km+ from rivers effected
USA					
Sophocleous et al. 1988	Arkansas river Kansas, USA	Experimental pump test	Increase in pumped nitrate from 1.8 to 5 mg/l over 8 day pump test.	-	Alluvial aquifer near river Kansas.

Table 11.6 Boreholes in the Lincolnshire Limestone abstracting water from nearby rivers

Source	River	Aquifer	River Bed deposit	Distance BH-river approx. (m)	Nitrate (mg/l)		Proportion of river water in discharge	Method of study Problems/ comments
					River	BH		
Ashby	Sprinwell brook	Lincs Limestone	?	400 m	-	?	?	Chilton and Shearer 1993
Drove Lane	River Slea	Lincs Limestone	Alluvial deposits overlie 5 - 10 m of clay of Upper Estuarine Series which overlies the limestone.	~ 350m	?	60 (1988)	?	In the Sleaford area a single surface and groundwater catchment may exist. (Alexander 1991) (Chilton and Shearer 1993)
Clay Hill	River Slea	Lincs Limestone	?	~350 m	?	40 (1980s)	?	Possible fault between BH and river. (Chilton and Shearer 1993)
Waneham Bridge	-	Lincs Limestone	?	?	?	80	?	Abstraction ceased 1992 (Chilton and Shearer 1993)
Moor Fm	-	Lincs Limestone	?	?	?	?	?	(Chilton and Shearer 1993)
Branston Booths	Heighington beck: cut through LST onto lower permeability layers, and intercepts recharge to aquifer, may lose to aquifer elsewhere	Lincs Limestone	?	~ 4.5 km faults between river and BH.	?	30 - 40 (1992) 50 (1988)	?	Some BH abandoned due to high nitrates. (GW nitrate levels 70-120 mg NO_3/l. (Chilton and Shearer 1993)

Note: Generally in the Lincs Limestone the relation of groundwater and surface water is uncertain. Springs in the east indicate outflow from the aquifer. Along the eastern edge of the outcrop: where most BH abstract, groundwater levels are lower in summer resulting in the drying up of springs. River infiltration occurs especially where rivers have permeable bed material, or where they pass over small, usually faulted outcrops of limestone (Chilton and

Table 11.7 Boreholes in the Chalk and Triassic Sandstone abstracting water from nearby rivers

Source	River	Aquifer	River Bed deposit	Distance BH-river (m)	Concentration of nitrate (mg N/l)		Proportion of river water in discharge	Method of study Problems/ comments
					River	BH		
Gatehampton	Thames	Chalk	0.5 m (0.4 - 0.45 m at bends) dark grey organic silt, (Younger 1990 1993)	~ 100 - 450	25	10 - 35	Chemistry: none (Robinson and Banks 1987) MODFLOW Modelling; (Charalambous et al. 1995) 41% av., up to 65%.	Modelling indicated river contribution, chemistry did not.
Hatton PS	Meece Brook	Triassic Sandstone	?	800	32 (1985)	33 (1985)	?	Hatton Catchment has mixture of arable and grassland.
Whitmore PS	Meece Brook	Triassic Sandstone	?	125	32 (1985)	30 (1985)	?	Nitrate concentrations in all boreholes rising.
Mill Meece PS	Meece Brook	Triassic Sandstone	?	450	32 (1985)	26 (1985)	? Nitrate levels in BH same as in river.	Brook nitrate varies seasonally and increases down stream. Modelled max. 45 mg/l
Dotton	River Otter	Triassic Sandstone	Dotton 3 connected to river by fractures	?	?	44 (in Dotton 1 &7)	?	Regional model, including regional nitrate model.

12. TECHNIQUES FOR IDENTIFICATION OF SOURCES OF GROUNDWATER NITRATE

12.1 Nitrogen Stable Isotopes

12.1.1 Sources of nitrogen in groundwater

Source identification of nitrate contamination in groundwater utilises the fact that the potential sources of nitrogen present are characterised by specific unique ranges of $\delta^{15}N$ isotopic signatures (Heaton 1986). Four main sources are generally recognised in relation to shallow unconfined aquifers (Green 1995).

1. Naturally mineralised soil organic nitrogen. The $\delta^{15}N$ signature of nitrate formed by this mechanism is dependent on which step during the conversion of organic N via NH_4 to NO_3 is rate determining. If NH_4 is present in excess then nitrification is the controlling process and the initial nitrate will be strongly depleted in ^{15}N. However nitrification is commonly rapid and the conversion of organic N to NH_4 is slow. This ammonification step is non-fractionating and the resulting nitrate will be similar to the parent nitrogen. $\delta^{15}N$ are typically found to be in the range +4 to +9 ‰ (Green 1995).

2. Inorganic fertilizers. Most commercial fertilizers are manufactured by fixation of atmospheric nitrogen and thus have $\delta^{15}N$ of around zero and always fall in the range +4 to -4 ‰. However relatively few studies have found that this light signature is retained in groundwater (Spalding et al. 1993, Gormly and Spalding 1979, Exner and Spalding 1994). It is more commonly retained in surface water bodies fed by direct run-off from fertilized fields.

3. Animal or sewage wastes. This is a diverse group of which the majority tend to be point sources where N occurs in the form of urea (Green 1995). This urea is subsequently hydrolysed to NH_4 and converted to NO_3. NH_3 is also lost to the atmosphere by volatilization and the remaining NH_4 becomes progressively enriched in ^{15}N. The signatures of such leachates are consistently greater than +10‰ and frequently exceed +20. Usually heavy signatures have been associated with the application of manure and slurry fertilizers (Aravena et al. 1993, Spalding et al. 1993) or are found beneath animal feedlots (Komor and Anderson 1993).

4. Precipitation. Published data on the concentration of nitrogen compounds in precipitation are scarce (Green 1995) but in general concentrations are low. In general the isotopic signatures are low, falling in the range -15 to +2 ‰. Heavier signatures are possible in rainwater contaminated by industrial pollutants.

These sources are summarised in Figure 12.1. Other potential sources were described by Hendry et al. (1984).

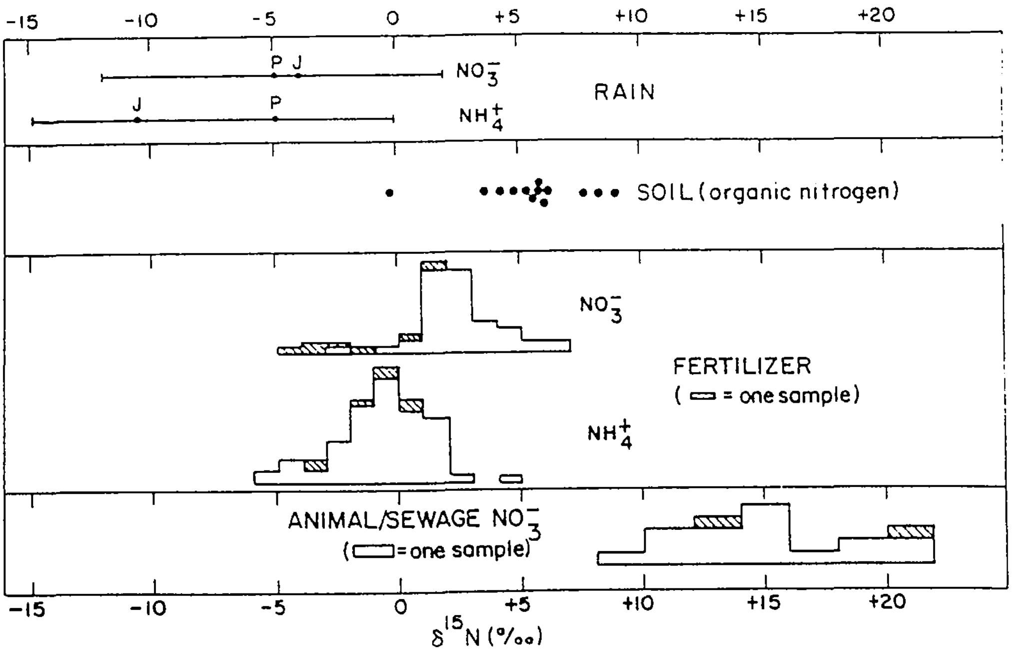

Figure 12.1 Potential sources of nitrate and their respective $\delta^{15}N$ isotopic signatures (from Heaton 1986)

12.1.2 Processes modifying source signatures

The idealised signatures shown above are frequently modified by the following processes active in the unsaturated and saturated zones which can make analysis of data extremely difficult.

1. Ammonia volatilization. This process can also cause a heavy signature within some inorganic fertilizers in the soil zone, where N is present in a reduced form. It is enhanced in calcareous soils with an elevated pH. Flipse et al. (1984) found a degree of enrichment sufficient to render the distinction between fertilizer and natural soil N impossible.

2. Denitrification. This is the microbiologically mediated process whereby ionic nitrogen oxides are reduced to nitrogen gases. It is always subject to a large kinetic fractionation effect whereby the lighter ^{14}N is lost preferentially to the gas phase. If denitrification alone is occurring a linear relationship between $\delta^{15}N$ and the natural log of concentration should be observed, and this has been observed in a semiconfined aquifer (Mariotti et al. 1988). A summary of calculated enrichment factors is given by Green (1995).

3. Nitrate reduction to ammonia. The implications of this process are not documented but it is thought to give a similar signature to denitrification.

4. Mixing. Many studies have used mixing to explain the observed isotopic signatures (Exner and Spalding 1994, Berndt 1990). It has been concluded by many researchers that intensively cultivated areas may be characterised by an agronomic source signature similar

to that of natural soil nitrogen due to the rapid homogenisation of sources by rapid crop growth and repeated ploughing.

12.1.3 Application to case studies

The method of stable isotopes has been successfully applied to a large number of nitrate problems, both in the USA and in Europe. The method is particularly good at distinguishing between inorganic fertilizer nitrogen and organic nitrogen derived from humans of animals. Waasennaar (1995) used a combination of nitrate ^{15}N and ^{18}O to determine both the origin and fate of nitrate. The results of these studies are summarised in Table 12.1.

12.2 Other Stable Isotopes

In a long term evaluation of the injection of treated wastewater into an alluvial aquifer, Bassett et al. (1995) investigated both boron concentration and stable isotope values as potential intrinsic tracers. The B stable isotopic values (δB) of background water (14‰) and water from anthropogenic sources such as treated municipal wastewater (6 - 10‰) and irrigation affected water (>40‰) were distinctly different. The B concentrations in combination with the B stable isotope values distinguished these water types plus natural saline recharge to groundwater. The authors stated that boron is suited for use as a conservative tracer in groundwater because of its high solubility, natural presence in nearly all water and lack of effects of volatilisation, redox reactions, and precipitation/ dissolution in most waters. This does not however take account of sorption.

12.3 Chemical Indicators

Chemical indicators have been relatively little used to date to distinguish between sources of nitrate in groundwater. Brandes (1974) used two radioactive tracers (tritium and ^{32}P) and sodium fluorescein in the outlets of septic tanks and found good correlations between the tritium and fluorescein and bacterial contamination of the water. However, it is preferable to use marker compounds already present. Ideal marker species have been defined by Rivers et al. (1996) as having the following characteristics:

- Presence in water indicates recharge from a specific source;
- Detectable in both groundwater and in recharge source water;
- Present in only one recharge source.

The problems are that generally such indicators are rare and are present in more than one recharge source. This necessitates a mass balance approach, where each species is accounted for in each recharge source.

Table 12.1 Application of nitrogen isotopes to case studies

Reference	Study area	N concentration (mg/l)/land use	$\delta^{15}N$ (‰)	Ascribed source
Kreitler et al. 1979	Long Island	east	+2 to +8	predominantly agricultural, possible some animal wastes
		west	+?	greater proportion of human waste
Gormly and Spalding 1979	Nebraska	10-30 /shallow water	+4 to +5	unfractionated fertilizer
		Deeper water	+5 to +7	fertilizer, denitrification
		?	>+9.5	animal wastes
Flipse et al. 1984	Long Island		+1.1 to +7.1	fertilization of lawns
Kaplan and Margaritz 1986	Israel	5 - 40, treated sewage infiltration	+19 to +29	denitrification of wastewater in treatment process
		agricultural area	-0.3 to +9	fertilizer/ natural soil nitrate
		livestock area	+9 to +11	some animal waste
		urban area	+4.5 to +8.4	not distinguishable
Mariotti et al. 1988	Chalk, N France	agricultural /unconfined	+3 to +7	fertilizers
		urbanised/unconfined	+8 to +13	urban wastes
		redox boundary	+24.1	denitrification
		confined	-7.4 to +1.3	natural soil nitrate
Aravena et al. 1993	Ontario	40 - 60	+8.1 to +13.9	septic tank leachate plume
		38	+3.4 to +6.2	agriculture, inorganic fertilizer, manure + soil organic N
Komor and Anderson 1993	Minnesota	1.5 /Uncultivated land	+2 to +6	natural soil nitrate
		Cultivated non-irrigated land	-2 to +6	inorganic fertilizer/ natural soil nitrate
		Residential - septic systems	+2 to +12	natural soil nitrate/ human waste
		Cultivated irrigated land	+1 to +23	inorganic fertilizer/ animal waste
		Feedlots	+5 to +43	animal wastes

Table 12.1 continued

Reference	Study area	N concentration (mg/l)/land use	$\delta_{15}N$ (‰)	Ascribed source
Spalding et al. 1993	Nebraska	Sludge disposal	+9 to +19	similar to sludge lagoon
Wilson et al. 1994	East Midlands Triassic Sandstone	0 - 10 7 2 - 10 7 - 11/ modern shallow recharge	-15 to -5 -5 to +5 +5 to +10 +23 to +31	ammonia fertilizers inorganic fertilizers natural soil nitrate farmyard slurry/ compost
Waasennar 1995	Abbotsford, Canada	Mean 10 mg/l, agriculture	+8 to +16	poultry manure
Green 1995	Jersey	High NO_2 High NO_3 Lower NO_3 ?	<+5 +5 to +7 +6 to +9 +10	rapid leaching of inorganic N non-point source agriculture (mainly inorganic) mixing with deep denitrified water, possible urban waste sewage treatment plant
Rivers et al. 1996	Nottingham Sherwood Sandstone	Shallow groundwater river water deep groundwater sewage	+13 to +17 +2.4 to +8 +4 to +8 +4	animal or sewage wastes fertilizers natural soil nitrate present as ammonia, no volatilisation

Gerritse et al. (1990) estimate a total household consumption of 4.5 kg of detergents per month. Laundry detergents are stated to contain 0.7 to 2.1% boron as sodium perborate and 0.1 to 0.6 fluorescent whitening agents. They used the boron to chloride ratio to show that boron was starting to enter groundwater. Natural organic material in water in their study area (Western Australia) interfered with the use of brighteners. Hanchar (1991) was able to detect optical brighteners in a spring down groundwater gradient of a dense area of unsewered sanitation, together with nitrogen and high coliform concentrations.

Lerner and Hoffman (1993) suggested that boron and phosphate are closely associated with sewage and could be searched for in existing groundwater quality data despite their widespread sorption by aquifer materials. Neither of these elements are routinely determined in the UK at present. Rivers et al. (1996) list previously used sewage markers as two optical brighteners (diaminostilbene disulphonic acid derivative and distyryl biphenyl derivative), synthetic oestrogen (from oral contraceptives), enterovirus and coprostanol. Particular compounds which could be targeted in the Nottingham area included sulphate (from dyers), cyanide (possibly from dyers and the food industry) and silver (from photographic industry). Preliminary work has shown that there is some indication of sewer leakage to groundwater in the Nottingham area from nitrate, ammonia and boron data. Sulphur and boron isotopes are both suggested as potentially useful indicators.

In a review of the impact of urban areas on groundwater quality, Rivers et al. (1996) compared the concentrations of a range of inorganic compounds in the rural and urban parts of their study area centred on Coventry (Figure 12.2). Those with the largest ratios, particularly chloride, zinc and boron, should be the most useful indicators of urban influence, but they are unlikely to permit the determination of the precise source of pollution. Nitrate itself may have less pronounced differential between rural and urban areas, as both urban and rural land uses contribute nitrate to the underlying groundwater. Possible sources indicated by inorganic markers include industrial activities and contaminated land, sewer leakage and other aspects of the urban environment such as parks, gardens, landfills and highway drainage.

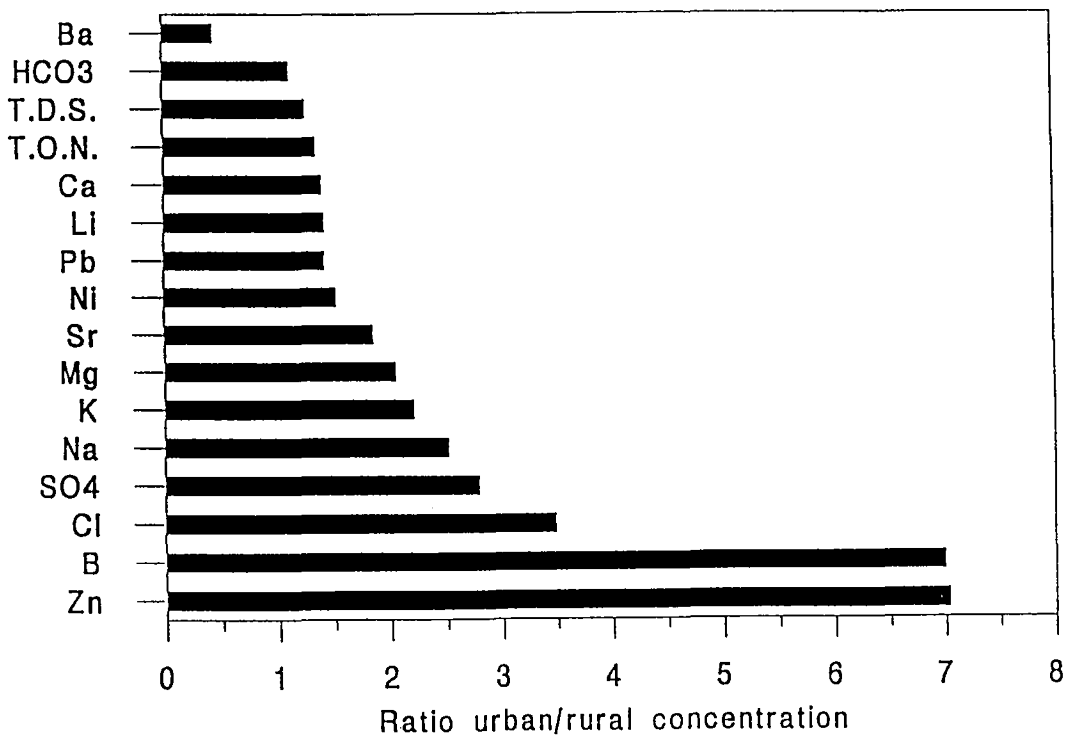

Figure 12.2 **Ratios of inorganic species in groundwater beneath rural and urban parts of the Coventry area (after Rivers et al. 1996)**

Ford and Tellam (1994) suggested that industry was responsible for many of the inorganic inputs to the groundwater beneath Birmingham, based on observed concentrations of metals in groundwater and their correlations between land use and local evidence of polluted groundwater. Nitrogen species were not highly correlated with land use, which may suggest multiple sources, including leaking sewers, or mixing. The groundwater sulphate concentrations in shallow groundwaters beneath Birmingham were too high to be derived only from sewer leakage, and must have reflected additional industrial inputs (Lerner et al. 1994).

In a current study of the urban geology of the Wolverhampton area, BGS has carried out limited groundwater sampling to see whether the impact of industrial activity could be determined. Background groundwater quality in the Triassic Sandstone is good, whereas that in the Coal Measures is less so, with elevated concentrations of chloride and sulphate. Groundwater samples from the urban part of the Triassic Sandstone aquifer showed strong positive correlations between chloride-nitrate, nitrate-boron and nitrate-chloride (Table 12.2), compared to the rural part. However, these correlations were based on a relatively small number of samples. Groundwaters from the Coal Measures gave low negative correlations (Table 12.3), suggesting that chloride and boron were probably derived from dissolution of the rock matrix, which is consistent with the more mineralised nature of Coal Measures rocks.

Table 12.2 Linear correlation coefficients between various chemical indicators in rural and urban areas of the Sherwood Sandstone beneath Wolverhampton and their concentration ranges

Indicator	Rural	Urban
$Cl:NO_3$	0.621	0.853
B:Cl	0.843	0.998
NO_3:B	0.771	0.825
Cl range (mg/l)	16.5-49.8	33.9-72.4
NO_3-N range (mg/l)	1.6-28.5	10.4-23.5
B range (mg/l)	10-150	70-80
Comment	Very wide range of B values. High NO_3-N from agriculture	Very positive correlations although this may reflect limited number of samples

Table 12.3 **Linear correlation coefficients between various chemical indicators in the Sherwood Sandstone and Caol Measures *beneath* Wolverhampton and their concentration ranges**

Indicator	Sherwood Sandstone	Upper Coal Measures	Coal Measures
	Rural/urban	Urban	Industrial
$Cl:NO_3$	0.792	0.935	-0.874
B:Cl	0.620	0.969	0.868
NO_3:B	0.903	0.969	-0.966
Cl range (mg/l)	16.5-72.4	26.3-135	60.8-81.8
NO_3-N range (mg/l)	1.6-28.5	2.4-22	<0.4-3.2
B range (mg/l)	20-150	30-470	130-1000
Comments	Combined data for rural and urban sandstone sites. High NO_3-N from agricultural activity	Cl, NO_3 and B all highly correlated most likely due to urban sewer leakage	High correlations with NO_3 due to lack of NO_3 in coal measures. High B from dissolution of aquifer

13. CATCHMENT STUDIES

The issue of the relative importance of non-agricultural sources can also be approached by reviewing the results of previous work assessing whole catchments. Gray and Morgan-Jones (1980) studied the nitrate concentrations in three adjacent Chalk groundwater sources in the Chilterns north of Slough. High concentrations of nitrate at one of these had prompted a more detailed study to identify the causes. The most likely major sources identified were fertilizer and sewage sludge applications to farmland in the catchment. Other activities such as septic tank discharges and urban development may have also contributed but these were similar over all three catchments studied and concentrations of nitrate in the other two remained lower. It was recommended that fertilizer application and sludge spreading be strictly controlled to see if the affected source would recover.

In the predominantly rural catchment of the Dyle, France, De Becker (1989) attempted a nitrogen budget for both ground and surface waters. He estimated that the principal inputs were from mineral fertilizers and animal wastes. The majority of this nitrogen was leached to groundwater and amounted to some 1490 tonnes/year. This produced an average concentration of about 5 mg N/l of nitrate throughout the catchment. By contrast unsewered sanitation accounted for only 70 tonnes/year but was unevenly distributed. The impact of population density could be seen in the significant correlation between groundwater sources containing nitrate concentrations of more than 10 mg N/l with areas having more than 10 inhabitants per hectare.

14. IMPORTANCE OF NON-AGRICULTURAL SOURCES

14.1 Scope and Scale in the United Kingdom

The preceding chapters have reviewed and summarised the technical aspects of each of the non-agricultural sources of nitrate identified in the study, and the methods which can be used to investigate their impacts on groundwater. For many of these sources, the national scope and scale is not well known, either in terms of the distribution and magnitude of the activity generating the nitrogen loading, or in terms of the observed impact on groundwater quality. In some cases, this lack of knowledge is purely a result of the technical difficulties in defining the scale of some of the sources. In others, those responsible for the operation and management of sources consider data to be more or less sensitive. This was anticipated for airfield de-icing. However, detailed and specific information about, for example, sewer leakage and sludge disposal to land is considered to be sensitive by the water industry and difficult to obtain. National groundwater quality monitoring is currently not adequate for the scale of impact on groundwater of non-agricultural sources of nitrate to be assessed. The EA's national approach to groundwater monitoring has been reviewed (Chilton and Milne 1994) and the proposed strategy is being adopted. Monitoring to support the implementation of the Nitrate Directive is one of the explicit objectives of the strategy.

An indication of the relative importance of the sources is provided by the amount of published material and current research devoted to each source. Thus, as shown in Table 1.1, atmospheric deposition has been recognised as important, has been extensively researched in the UK, and is now relatively well characterised. With tighter controls on atmospheric pollution and vehicle emissions, this may become a more restricted source in the future. Leaking sewers and sludge application to land are important and likely to become more so; this is reflected in the recent and current research interest (Table 1.1).

Table 14.1 summarises the research results which have been located by the literature survey in the present project. The three columns, application rate or loading, leaching losses and observed nitrate concentrations in the underlying groundwater are the pieces of information required for evaluating the importance of each of the non-agricultural sources. It is clear from Table 14.1 that data are lacking in many areas, and Table 14.2 summarises the most significant areas of remaining uncertainty for each of the non-agricultural nitrate sources. Information on the scope and extent of each source would enable them to be ranked in importance nationally, and for their position in the overall nitrogen budget for NVZs or potential NVZs to be assessed. At a catchment scale, assessment of the impact or contribution from several possible sources would require knowledge of the area affected and the hydraulic loading or surcharge associated with each potential source.

From Tables 1.1 and 14.1 and the information presented in the respective review chapters, leaking sewers in urban and suburban areas and sludge application to land over significant aquifers appear to be the most important non-agricultural sources. Both are widespread but difficult to quantify. It is clear from the research results described in Chapter 6 that nitrate leaching losses from land to which significant amounts of sludge have been applied can be very high, and could produce nitrate concentrations in the underlying groundwater well in excess of 11.3 mg NO_3-N/l (Table 14.1). The importance of this source would depend on the area of land so used in the catchment. Land

Table 14.1 Summary of published research findings.

Nitrogen source	Loading or application rate (kg N/ha/a)	Leaching losses (kg N/ha/a) or Effluent concentration (mg/l)	Associated groundwater nitrate concentration (mg NO_3-N/l)	Approach used	Reference
Atmospheric deposition	5 - 35	-	-	rainfall sampling (wet deposition) modelling (dry deposition)	DoE 1994
Land application of sewage sludge	150 - 700	40 - 150 (kg/ha/a) (40 - 80 mg NO_3-N/l)	?	lysimeters	Shepherd 1994
Losing rivers	N/A	river 7 mg NO_3-N/l	7	sampling modelling	Hatton study, Gatehampton 1988
Septic tanks	population density 2 - 25/ha	N concentration of wastewater 20-100 mg NO_3- N/l	8-40	Estimate of leaching mass balance groundwater sampling	Foster & Hirata 1988 Hantzsche & Finnemore 1992 Postma et al. 1992)
Leaking sewers	-	NH_4 32 - 132 mg/l (no nitrate)	10-100	multi-level sampler	Rettinger et al. 1991
Highway drainage	3 - 5	0.2 - 3 mg NO_3-N/l in runoff	1-3	direct sampling	Luker and Montague 1994
Landfills	N/A	NH_4 30 - 115 mg/l(no nitrate)	0-2	multi-level sampling	Bjerg et al. 1995
Recreational fertilizer use	80 - 200	?	?	lysimeters	Lawson 1991
	25 - 480	0 - 63 kg/ha N (0 -18.9 mg/l NO_3-N)	?	lysimeters	Petrovic 1989 (summary of field expts)
Airfield deicing	RAF Waddington: ca. 11800 kg N (area of airfield unknown)	ca. 11800 kg N (area of airfield unknown)		"worst case" estimate	NRA?
Intensive livestock	420	?	?		Worthington & Danks 1992
Silage clamps	N/A	?	?		
Slurry storage	N/A	unsaturated zone 37-68 mg NO_3-N/l	?	core profile porous pots	Gooddy et al. 1994 Korom & Jeppson 1994
Effluent recharge	-	10-20 mg NO_3-N/l	2-5 mg NO_3-N/	Sampling of effluent and groundwater	Bouwer & Rice 1984

application of sewage sludge should be controlled in the Zone 2 areas of supply catchments and in any case following Code of Good Agricultural Practice for the Protection of Water (MAFF 1991) should prevent excessive applications. Neither of these two potential sources of groundwater nitrate can be adequately characterised without the assistance of the water utilities (Table 14.2).

Septic tank systems have limited usage in England and Wales and, in contrast to other countries quoted in Chapter 2, are unlikely to be a major source of groundwater nitrate. While the hydraulic loadings and nitrate leaching can be significant, population densities in rural areas where these are used are likely to be much lower than in the studies quoted in Chapter 2. In some cases, individual septic tanks may be providing a contribution to groundwater nitrate, but this is likely to affect only a very small proportion an NVZ.

The complexities of the interaction between a river and the underlying aquifer are well illustrated in Chapter 11. Where there is scope for exchange of water and solutes between surface water and groundwater, then it is clear that the quality of the latter could be affected. Where the river contains a significant component of sewage treatment effluent and river nitrate is high during the winter, then this effect could include an increase in nitrate concentration, although the one example quoted in chapter 11 suggested that the contribution from this source was very small compared to the agricultural inputs over the remainder of the catchment.

The other potential sources listed in Table 14.1 are likely to be relatively modest on an overall national scale, but could be important at the supply catchment scale. Significant leaching of nitrate may occur beneath the most intensively fertilized recreational turf areas, but these are likely to be a very small proportion of any catchment land area. Most recreational areas, such as school and council playing fields are likely to have more modest fertilizer applications. Airfield de-icing and landfills could be important where they occur, but are likely to be restricted to few catchments. The use of urea-based de-icing compounds is being phased out by civil airport authorities, partly on environmental grounds, and their usage at military airfields in NVZs may be discontinued in due course by the Ministry of Defence.

Table 14.2 Ranking of non-agricultural nitrogen sources and areas of uncertainty

Nitrogen Source	Area of Uncertainty	
	Technical/Scientific	Scale
Leaking sewers	Hydraulic loading, nitrogen content and nitrogen mobilisation, use of tracers	Yes, unknown extent (Plc information sensitive)
Land application of sewage sludge	Nitrate mobilisation, use of tracers	Yes, current and future scale (Plc information sensitive)
Losing rivers	Modelling, tracers, denitrification	Yes, spatial and seasonal uncertainty
Highway drainage	No major areas, hydraulic loading	No, catchment survey
Landfills	N oxidation and mobilisation, tracers	No, catchment survey
Septic tanks	Proportion of N oxidised and mobilised	Not major, depends on population or installation density
Recreational fertilizer use	No major areas of uncertainty	No, catchment survey
Atmospheric deposition	No major areas of uncertainty	No major areas of uncertainty
Airfield deicing	Proportion which runs off, N mobilisation, use of tracers	Yes, military usage unknown, catchment survey
Intensive livestock	Leaching losses	No, catchment survey
Silage clamps	N mobilisation	No, catchment survey
Slurry storage	N mobilisation	No, catchment survey
Effluent recharge	Use of tracers	No, catchment survey

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