

# ***WORKING PAPER***

**THE ENVIRONMENTAL EFFECTS OF THE  
INTENSIVE APPLICATION OF NITROGEN  
FERTILIZERS IN WESTERN EUROPE:  
PAST PROBLEMS AND FUTURE PROSPECTS**

*Philippe Souchu  
Didier Etchanchu*

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WP-89-04

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## Foreword

Agriculture, along with energy and materials use, is one of the three key sectors of human economic activity that is currently causing many environmental problems in Europe. The focus of this study is on the effects resulting from the excessive use of synthetic nitrogen fertilizers, and the inefficient use of animal manure as a source of fertilizer. Numerous studies have identified the leaching of nitrogen into aquatic systems as the cause of dangerously high levels of nitrates in drinking waters, eutrophication and anoxia in surface waters, and disruption of the food web in coastal marine waters. This study not only cites the current problems, but also provides an evolutionary perspective, based on an analysis of past problems, the processes which shape the kind of changes that have occurred, and a scenario of problems that might emerge in the future.

Current agricultural problems exist because farmers, and agricultural planners in government and the agro-industry focussed too much attention on the benefits of intensive application of nitrogen fertilizers (i.e., spectacular increases in yields of agricultural crops), and did not foresee the environmental problems caused by intensification. The authors of this paper project the effects of fertilizer use to the year 2010, based on the assumption that current trends will continue. They clearly demonstrate that such a trend is not ecologically sustainable, and analyze how future problems can be mitigated by the use of new technologies, and strategies for the more efficient use of animal manure.

This paper is a valuable contribution to IIASA's study, *The Future Environments for Europe: Some Implications for Alternative Development Paths*.

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## **1. INTRODUCTION**

Over the last several decades, considerable attention has been focused on the influence of intensive nitrogen fertilization on the quality of the aqueous environments. Currently, there is no doubt that the use of chemical fertilizers and animal manure in Europe is the major cause of nitrate accumulation in fresh and marine waters.

The first goal of this work is to study the processes of nitrogen transfer from agricultural soils to coastal environments, and to review the main problems caused by excessive inputs of nitrogen.

The second goal of the study is to review the changes that have occurred in the past and to define current trends. In the last part of this work, we provide scenarios of possible changes in the next century. What will the environmental consequences be if current trends continue? What provisions could be made in order to reduce nitrogen losses to the environment while maintaining agricultural productivity? Should these measures limit the losses of nitrogen or should they limit the inputs? What could be the contribution of new technologies in mitigating the problem?

## 2. PROCESSES OF CHANGE

### 2.1. Soils

#### 2.1.1. Inputs

##### 2.1.1.1. Inorganic nitrogenous fertilizers

The most commonly applied N-fertilizers in European agriculture are ammonium nitrate (with the highest nitrogen content), urea, ammonium sulfate and ammonium phosphate. In most European countries, annual application rates of chemical fertilizers exceed 70 kg N ha<sup>-1</sup> of agricultural area, while in the U.S.A. the mean value is 23 kg N ha<sup>-1</sup> (Table 1). The biggest consumers are the Netherlands (238 kg N ha<sup>-1</sup>) and Denmark (147 kg N ha<sup>-1</sup>).

Table 1. Annual consumption of N-fertilizer in various European countries.

Country	kg N ha <sup>-1</sup>
Netherlands	238
Denmark	147
Belgium	132
Luxembourg	122
F.R.G.	114
G.D.R.	111
Hungary	95
U.K.	86
France	74
Poland	70
Sweden	70
Italy	58
Ireland	57
Greece	45
U.S.A.	23

##### 2.1.1.2. Animal manure

Animal manure is the second most important source of nitrogen in European agriculture, and sometimes the primary one in areas of intensive livestock breeding (e.g., 60% of the inputs in Belgium). The chemical composition of manure is different for each animal species (Table 2). An important fraction of nitrogen is in organic form which is partly mineralized during the year of application. In most manure the main mineral fraction is in ammonium form (NH<sub>4</sub><sup>+</sup> - N) and represents 40 to 70% of the total nitrogen content.

Application rates of animal manure are generally calculated from the number of animals, and from tables giving the mean quantity of nitrogen produced per animal for a given species (Table 3).

Table 2. Distribution (%) of nitrogen in animal manure (C.C.E., 1978 and references cited therein).  $N_m$  is the mineralized fraction ( $NH_4^+$  - N, urea, uric acid);  $N_e$  is the organic fraction that is mineralized during the year of manure application;  $N_r$  is the residual organic fraction--the nitrogen content is only released during the years following the year of manure application.

Type of Fertilizer	$N_m$	$N_e$	$N_r$
Liquid manure of cattle	40	30	30
Liquid manure of pigs	50	22	28
Liquid manure of poultry	70	20	10
Liquid manure of calves	80	9	11

Table 3. Amount of nitrogen in animal manure for each animal species per animal per year (Treguer, 1984).

Cattle	89 kg
Pigs	10 kg
Poultry	0.24 kg
Sheep	4 kg

### 2.1.1.3. Atmospheric precipitation

#### *Wet precipitation*

High concentrations of  $NO_3^-$  - N and  $NH_4^+$  - N can be found in rainfall, not only in industrial regions, but also in agricultural areas. Mean annual concentrations of ammonium in wet precipitation vary from 20-100  $\mu\text{mol l}^{-1}$  in Europe with a maximum in the Netherlands (Figure 1), while nitrate concentrations vary on average between 2-16  $\mu\text{mol l}^{-1}$  (Figure 2).

#### *Dry deposition*

Dry deposition of particulate and gaseous nitrogenous compounds also occurs, mainly  $NH_4^+$  -  $NO_3^-$  in fine particles, and  $NH_3$ , respectively. They represent about 50% of the total deposition of  $NH_3$  and  $NH_4^+$  in Europe (Asman and Janssen, 1986).

#### *Total deposition*

According to Grennfelt and Hultberg (1986), the total deposition of nitrogen (wet and dry) is as high as 30 to 40  $\text{kg N ha}^{-1} \text{ yr}^{-1}$  in many areas in Central Europe. The estimate calculated from the data given by Asman and Janssen (1986) is about 10  $\text{kg N ha}^{-1}$  for Western Europe.

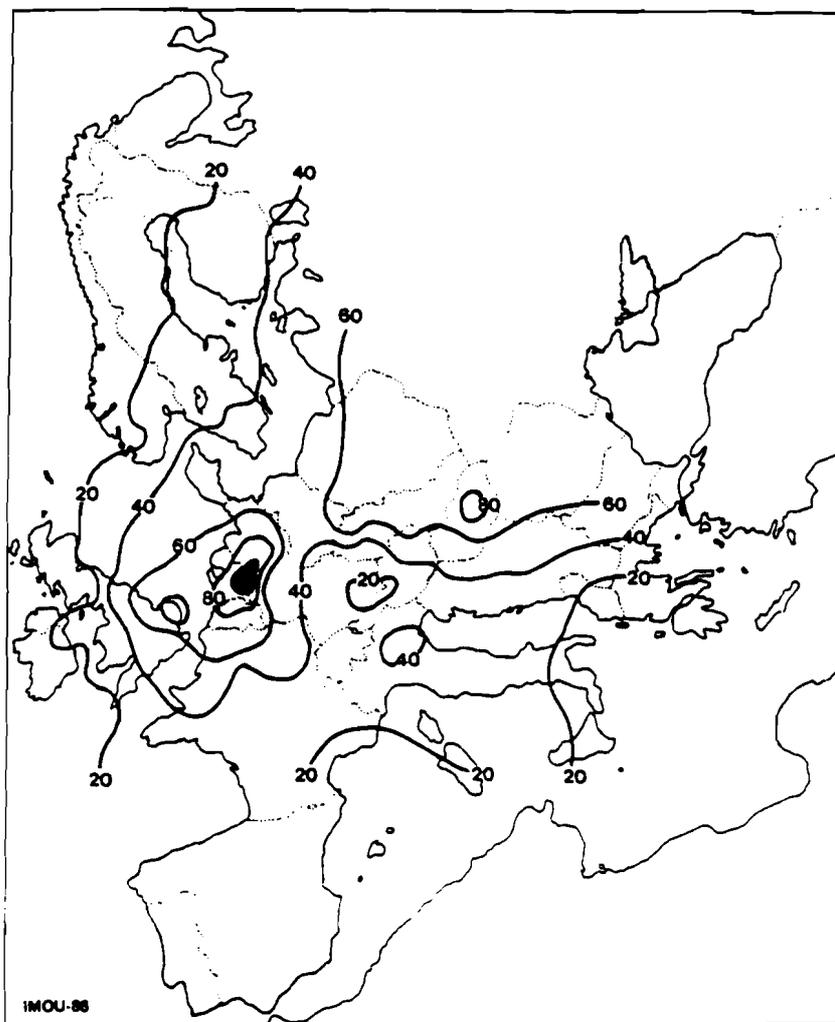


Figure 1 Measured  $\text{NH}_4^+$  concentrations in precipitation in Europe ( $\mu\text{mol l}^{-1}$ ) (Asman and Janssen, 1986).

#### 2.1.1.4. $\text{N}_2$ biological fixation

$\text{N}_2$  fixation is the conversion of atmospheric  $\text{N}_2$  to ammonium. The most important  $\text{N}_2$  fixing organisms belong to the bacterial genus *Rhizobium*, which occur within the roots of leguminous plants (clover, lucerne, etc.). These bacteria, through the activity of the enzyme "nitrogenase", fix  $\text{N}_2$  in symbiosis with the legume.

The amount of  $\text{N}_2$  fixed by leguminous plants can reach 200 or 300  $\text{kg N ha}^{-1} \text{yr}^{-1}$  according to the species, whereas cereals generally fix less than 10  $\text{kg ha}^{-1} \text{yr}^{-1}$  (Royal Society, 1983.) The total amount of nitrogen fixed in soils may therefore be calculated from the areas covered by the leguminous plants. This input probably represents about 7  $\text{kg ha}^{-1} \text{yr}^{-1}$  on average in Europe (i.e. 7% of the total input of nitrogen on agricultural soils).

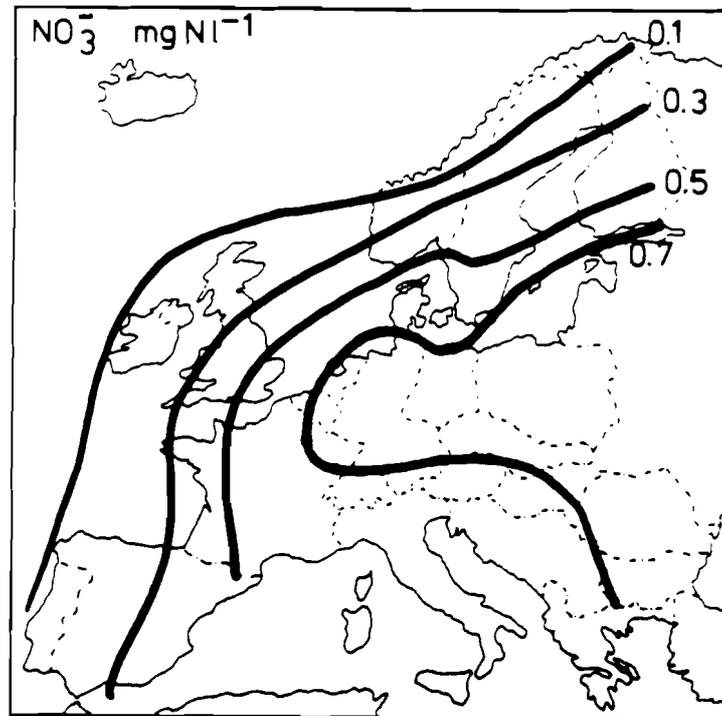


Figure 2 Measured  $\text{NO}_3^-$  concentrations in precipitation in Europe (Nodop, 1986).

## 2.1.2. Outputs

### 2.1.2.1. Plant uptake

Nitrogen uptake by crops may be calculated from the specific N-content for a given plant (Table 4), and from statistical data on the plant production (Yearbook of Agricultural Statistics, 1985). The mean annual nitrogen output by crops in Europe is therefore estimated at about  $47 \text{ kg ha}^{-1}$  of total area or  $77 \text{ kg ha}^{-1}$  of agricultural area.

### 2.1.2.2. Ammonia volatilization

A substantial volatilization of ammonia (about 10% on average) occurs in agricultural soils. Emissions are highest from livestock manure applied on grassland and arable land, but also occur from ammonium fertilizer application. According to Buijsman, et al., (1985), 81% of the total ammonia emissions in Europe is due to domestic animals (mainly cattle), 17% to chemical fertilizer and only 2% to industry. Volatilization is therefore often calculated from the number animals and from known  $\text{NH}_4^+$ -emission rates for each type of manure. The mean European ammonia emissions are about  $10 \text{ kg ha}^{-1} \text{ yr}^{-1}$  of total area ( $16 \text{ kg ha}^{-1} \text{ yr}^{-1}$  of agricultural area). However, some important spatial differentiation occurs owing to the type of manure and fertilizer applied, and also to the pH of the soil on which they are applied. For instance, the volatilization rate is higher when fertilizers are applied on calcareous soils with high pH values.

### 2.1.2.3. Denitrification

Denitrification is the conversion of nitrate to gaseous nitrogenous products. The major end product of denitrification is  $\text{N}_2$ , but nitrous oxide ( $\text{NO}_2$ ) may also be an important product under acid conditions ( $\text{pH} < 5$ ) and low temperatures ( $T < 5^\circ\text{C}$ ). Up to 6% of the

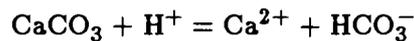
Table 4. Nitrogen content in cultivated plants in the United Kingdom (Royal Society, 1983).

Crop	Production (kt)
<i>Grass and Lucerne</i>	
Silage	22148
Hay <sup>a)</sup>	7000
Dried grass	150
Grazed <sup>a)</sup>	18963
Rough grazing <sup>a)</sup>	9495
Arable silage	350
<i>Straw</i>	
Burnt + baled	
<i>Grain</i>	
Wheat	6450
Barley	9830
Oats	715
Mixed corn	65
Rye	30
Maize	3
<i>Fodder Crops</i>	
Beans: stockfeed	120
Turnips, swedes & fodderbeet	5520
Mangolds	448
Maize (green)	923
Rape (stockfeed)	545
Kale, cabbage etc.	2157
<i>Roots and Vegetables</i>	
Potatoes	7289
Brussels sprouts	206
Cabbage & cauliflower	1073
Carrots	735
Parsnips	77
Turnips & swedes	215
Beetroot	116
Onion	305
Leeks	38
Beans (broad,runner and french)	155
Peas	325
Celery	70
Lettuce	137
Rhubarb	43
<i>Fruit</i>	
Apples	398
Pears	31
Other top fruit	31
Soft fruit	97
<i>Other Crops</i>	
Sugar beet	7081
tops	1260
Rape, oilseed	155
Hops	9
bines (burnt)	

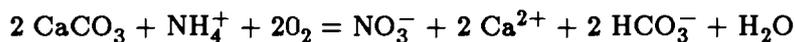
a) These are dry matter values.

total N in soils is released by denitrification. The denitrification process occurs under conditions of reduced oxygen supply, generally in subsoils with low permeability. The denitrification rate is therefore strongly influenced by the level of the water table since wet soils generally have a more limited oxygen supply.

The denitrification rate also depends on the pH of the soils. If pH is higher than 7 under aerobic conditions,  $\text{NH}_4^+$  is easily oxidized into  $\text{NO}_3^-$  which is a stable form in water (Egboka, 1984). The nitrification process can therefore occur in soils with high pH values, for example, in calcareous media. Nitrification of ammonium fertilizers ( $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ ) applied on these soils releases protons ( $\text{H}^+$ ) which may contribute to carbonate dissolution (Faurie, 1977; Durand, 1978) according to the following equations:



Thus the overall equation can be written as follows:



Probst (1983) has shown for a calcareous Molasse basin of southwest France, that 30% of the total carbonate dissolution may be attributed to the N-fertilizer application. In the same way, the increasing application of nitrogenous fertilizers on agricultural soils of the Garonne basin is responsible for an increase of 1% per year of the total carbonate dissolution (Etchanchu, 1987). When all the carbonates of the upper layers of the soils are dissolved and leached, then clays become sensitive to the lixiviation, the structural stability of the soils decreases and mechanical erosion is accelerated.

#### 2.1.2.4. Leaching

Leaching is a major source of  $\text{NO}_3^-$  - N loss from soils when excessive amounts of fertilizer are applied. Currently in Europe, approximately one third of the total N applied as fertilizer and manure is leached to the groundwater. This loss occurs by different pathways:

- 1) Water infiltrates through the unsaturated zone and into a zone containing high concentrations of nitrate.
- 2) Water is drained to rivers via channels. This flow component, sometimes called "subsurface runoff" or "interflow", often contains more nitrate than groundwater (Probst, 1985; Etchanchu, 1987).
- 3) In a less important pathway, water moves on the soil surface and in microchannels (during flooding), and quickly reaches macrochannels and rivers. It is called "surface runoff" or "quick return flow", and mainly carries nitrogen in organic particulate form.

#### *Methods to calculate the leaching:*

Estimation of nitrogen losses by leaching is difficult. Several methods have been used to determine this loss, the easiest of which is the extrapolation of leaching from the nitrate concentrations measured in upstream waters (Billen et al., 1985 a,b). However, this method underestimates the process, in our opinion, because denitrification may occur between groundwater and river water.

A better method is to estimate nitrate by direct measurement in drainage waters, but this requires extensive sampling because of the great heterogeneity of concentrations

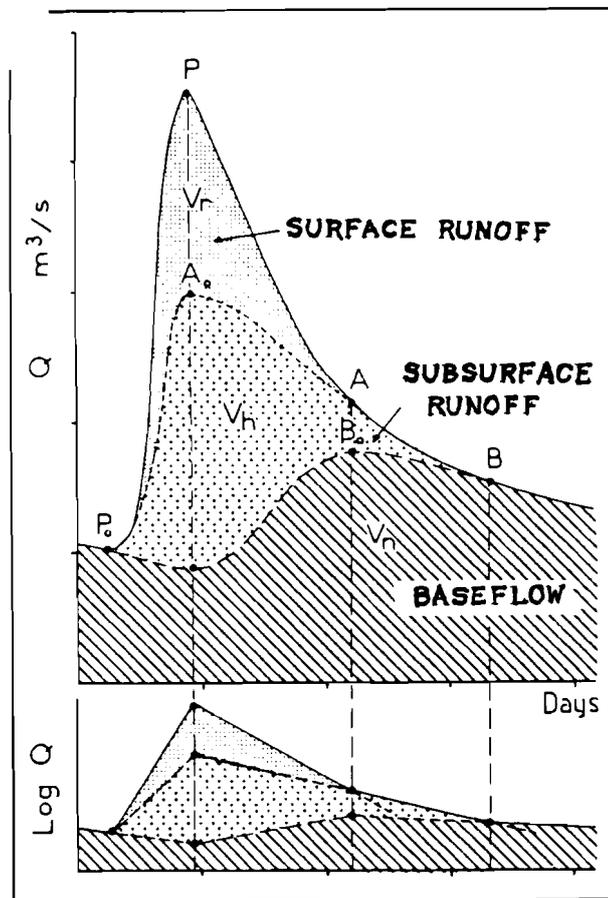
found in drainage waters.

Some authors also use the  $\text{NO}_3^- - \text{N}/\text{Cl}$  ratio, measured at different depths in the soil profile, in order to distinguish leaching and denitrification. The ratio remains unchanged if the loss is only through leaching, but decreases if denitrification occurs (Yusop, et. al, 1984).

Another method, proposed by Probst (1983, 1985), assumes that during storm runoff events, the streamflow is a mixture of three different components: surface runoff, subsurface runoff and ground water flow or baseflow. Assuming that nitrate concentrations are constant in each reservoir, and that relative contributions of each reservoir change during a storm runoff period, the stream hydrograph can be subdivided into three separate flow components. The separation is based on the identification of the different components on the falling curve of the hydrograph (Figure 3). A simple mixing model is then used, based on hydrological and geochemical mixing of waters coming from different reservoirs:

$$C_t \cdot Q_t = C_1 \cdot Q_1 + C_2 \cdot Q_2 + C_3 \cdot Q_3 ;$$

C being the  $\text{NO}_3^-$  concentration, Q the water discharge, index t the total streamflow at the outlet, and the numbers 1, 2, 3, the different flow components.



**Figure 3** Separation of the different flow components on the storm hydrograph (Probst and Bazerbachi, 1986).

Such an equation can be written for each sampling time. Discharges and concentrations are measured at the outlet of the basin. The discharges of the different flow components are estimated from the differentiation of hydrograph separations (Figure 3), and the nitrate concentration in each flow is calculated by solving a system of  $n$  equations ( $n$ =number of samples), and three unknowns (the three components) by a multivariate linear regression (least squares method). The main advantage of this method is to give a general idea of the mechanisms of nitrate transfer in an agricultural watershed.

For instance, in the Girou watershed (Garonne) during the hydrological year 1983-1984, the mean annual concentrations of nitrate found by this method were  $50 \text{ mg l}^{-1}$  in subsurface runoff,  $38 \text{ mg l}^{-1}$  in groundwater and  $16 \text{ mg l}^{-1}$  in surface runoff. Since groundwater, subsurface runoff and surface runoff accounted for 73%, 19% and 8% of the total water discharge respectively, their contributions to the total nitrogen load in the river were 72%, 25% and 3% (Etchanchu, 1987).

#### *Factors influencing leaching*

The rate of nitrate leaching depends on many factors, for example, climate (rainfall), application rate of fertilizers and type of fertilizer, rate of irrigation (especially when using sewage effluents), soil properties (texture, pH) and crop cover.

It has also been shown that the use of organic manure might increase the biomass of microorganisms and consequently induce a significant decrease, by the denitrification process, in the amount of nitrate leached by the soil. Nitrate pollution could therefore be significantly decreased by combining chemical fertilizer with organic manure in appropriate proportions (Alfoldi, 1983). In the same way certain reducing materials could increase the reducing capacity of the soil, for example manure applied with pyrite and lignite content (Alfoldi, 1983).

Soil properties also have an important role in the denitrification process. The soil texture directly influences both the level of the water table and the redox potential. Denitrification is of minor importance in well aerated sandy soils, but becomes important in heavy-textured soils. According to Gustafson (1983), sandy soils lose more than twice as much nitrogen compared with the clay soils, primarily because the root depth is more shallow in the sandy soils and nitrogen below that depth is not available for the crop. The ability of soils to reduce nitrates depends on the thickness of the unsaturated zone which forms an open oxidation system (Champ, et al., 1979; Alfoldi, 1983). In the saturated zone, and in clay soils with anaerobic conditions, this ability also relates to the ferrous iron - nitrate redox system (Gustafson, 1983) and the quantity of oxidizable carbon (Egboka, 1984).

The climate, and more specifically, the amount and distribution of precipitation, is one of the main factors influencing nitrate leaching. As will be demonstrated later, the amount of nitrate leached is well-correlated with runoff, especially if runoff occurs during or right after the application period of N-fertilizer.

In conclusion, more than  $90 \text{ kg N ha}^{-1}$  enter the soils annually from various sources in Western Europe. Among them, N-fertilizer application accounts for 49%, manure application for 33%, precipitation for 11%, and  $\text{N}_2$  fixation from the atmosphere 7%. Plant uptake of nitrogen from European agricultural soils is 52%; 48% of the nitrogen is lost to the environment (27% through leaching into groundwater and river waters, 21% through denitrification and volatilization). Thus, nitrogen output from soils is closely linked to fertilizer and manure application rates.

### 2.1.3. Relationships between input and output in European agricultural soils

Several river basins were selected for evaluation of the impact of agricultural inputs on nitrogen losses to the environment. In addition, an evaluation was made on the national scale for three countries. Included were the following:

- 1) Two French basins:
  - a) The Aulne basin (1800 km<sup>2</sup> with 67% of agricultural area, (AA); Souchu, 1986 a,b).
  - b) The Garonne basin (55,000km<sup>2</sup> with 47% of AA; Etchanchu, 1987).
- 2) Three Belgian basins (Billen et al., 1985 a,b):
  - a) The Scheldt basin (12,600km<sup>2</sup>) with 46% AA.
  - b) The Meuse basin (13,900km<sup>2</sup>) with 41% of AA.
  - c) The Yser basin (1100km<sup>2</sup>) with 68% of AA.
- 3) Three countries:
  - a) Belgium (30,500km<sup>2</sup>, 46% AA; Billen et al., 1983).
  - b) United Kingdom (245,000km<sup>2</sup>, 75% AA, with a large grassland area; Royal Society, 1983.)
  - c) Denmark (43,000km<sup>2</sup>, 67% AA; Schroder, 1985.)

Table 5 presents data on the nitrogen budgets in the agricultural soils of these areas. Additional data were analyzed to establish the relation between NO<sub>3</sub><sup>-</sup> concentrations in river waters and fertilizer input; these data were for the Tisza river in Hungary, the Moselle river (Kattan, et al., 1986) and the Girou river (Etchanchu, 1987) in France, the Odense river in Denmark (Hagebro, et al., 1983), and, at the national scale, for England, Scotland, and Ireland (Royal Society, 1983).

A strong positive linear relationship was shown between the total nitrogen output by plant uptake and the application rate of N-fertilizer and manure on soils (Figures 4 and 5). Although application of N-fertilizer undoubtedly has a positive impact on agricultural productivity, we can see that the application rate of fertilizer and manure has to be increased by a factor of 4.6 (from 50 to 230 kg ha<sup>-1</sup>) in order to produce a three-fold increase in production. We may assume that, for higher application rates of fertilizer, the plant uptake could then reach a maximum after which the relationship is no longer linear, but rather is a logarithmic one.

As we can see in Figure 4, the mean European values for N-fertilizer application and plant uptake (2), calculated from the data of the Agricultural Yearbook is lower than the mean values calculated for the selected basins (1). In fact, these basins are under more intensive agriculture than the average of the European countries.

On the other hand, a good relationship was also found between N-fertilizer input and nitrate leaching ( $r = 0.92$ ; Figure 6) as well as nitrate concentrations in river water ( $r = 0.92$ ; Figures 7 and 8). The higher the fertilization rate, the higher the losses by nitrate leaching and the higher the concentrations in groundwater and river water. The increase of N-fertilization rate by a factor of 2 (from 65 to 130 kg N ha<sup>-1</sup>) results in a three-fold increase in leaching and a more than two-fold increase in nitrate concentration in river waters. The discharge of nitrate by rivers to coastal waters is therefore doubled (Figure 9).

The relation between fertilizer input and leaching shows that there is no leaching when the application rate of chemical fertilizer is less than 37 kg N ha<sup>-1</sup> (of agricultural area). In fact, leaching does occur below this value. The relationship between fertilizer

Table 5. Nitrogen budget in agricultural soils of several basins and countries in Europe.

	Garonne	Aulne	Scheldt	Meuse	Yser	Belgium 1980	UK 1978	Denmark 1980
in kg ha <sup>-1</sup> of total area								
N-Fertilizer	32.0	66.7	77.7	30.2	100.0	60.3	47.0	87.1
Manure	29.1	116.7	94.4	61.1	136.0	107.9	41.6	73.0
Total fertilizer	61.1	183.4	172.1	91.3	236.0	168.2	88.6	160.1
Precipitation	8.3	3.9	11.1	7.9	12.7	11.3	11.7	10.0
N <sub>2</sub> Fixation	3.8	1.7					6.4	6.7
Crops	35.2	94.4	107.1	63.3	127.0	81.0	55.5	77.0
Leaching	15.4	44.4	7.9	7.9	14.5	7.8	13.9	64.0
Volatilization	13.4	22.2	24.2	16.5	37.0	26.8	22.4	38.0
Denitrification	9.1	27.7	43.2	11.5	67.5	64.2	14.9	20.0
in % of the total input and output								
	Garonne	Aulne	Scheldt	Meuse	Yser	Belgium 1980	UK 1978	Denmark 1980
N-Fertilizer	44	35	42	31	40	34	44	49
Manure	40	62	52	61	55	60	39	41
Total fertilizer	84	97	94	92	95	94	83	90
Precipitation	11	2	6	8	5	6	11	6
N <sub>2</sub> Fixation	5	1					6	4
Crops	48	50	58	64	51	45	52	39
Leaching	21	23	5	8	6	5	13	32
Volatilization	18	12	13	16	15	15	21	19
Denitrification	13	15	24	12	27	35	14	10

and leaching would be probably non-linear if there were data corresponding to low application rates of chemical fertilizer.

The strong correlation between volatilization of NH<sub>3</sub> and manure application rate is logical (Figure 10), since the volatilization is generally calculated from the number of animals and the amount of manure emitted by each species.

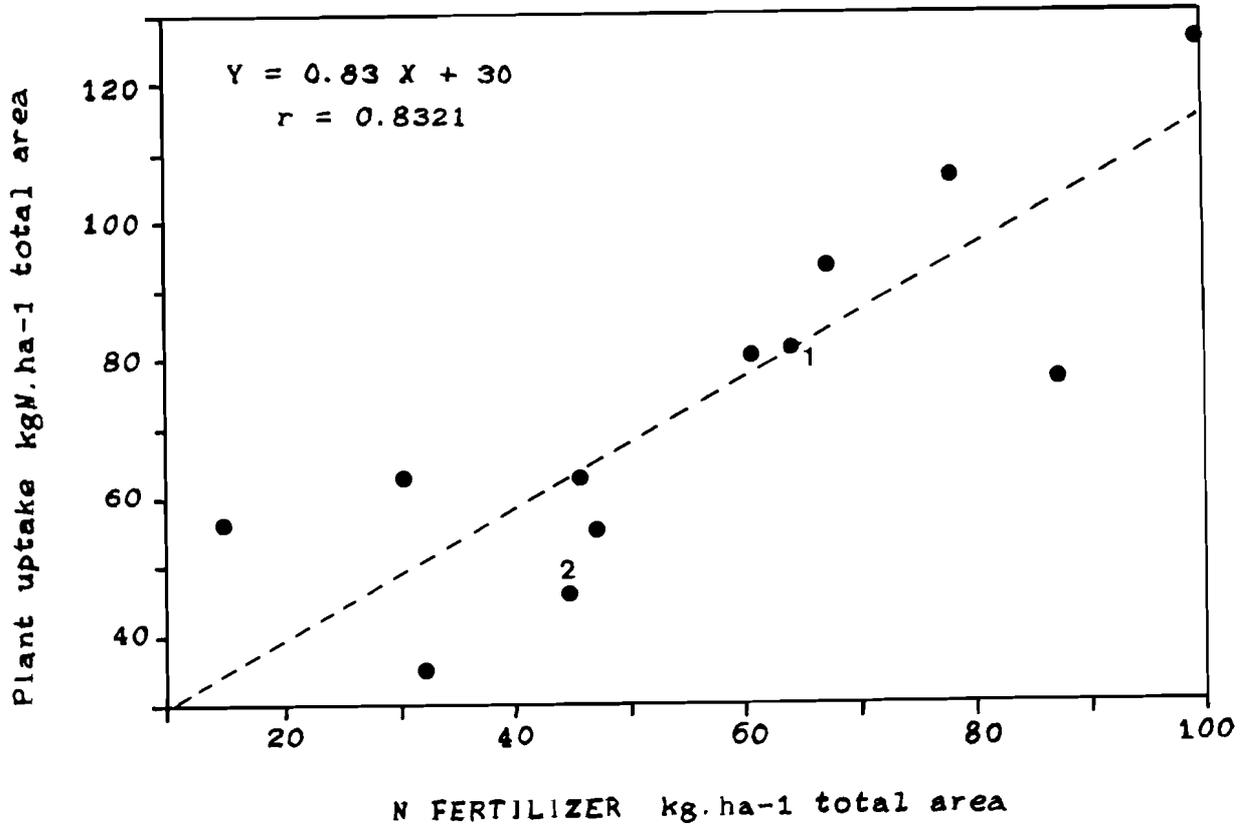


Figure 4 Plant uptake versus chemical fertilizer application rate. Number 1 signifies the average for the 8 basins of Table 5. Number 2 is the mean European value.

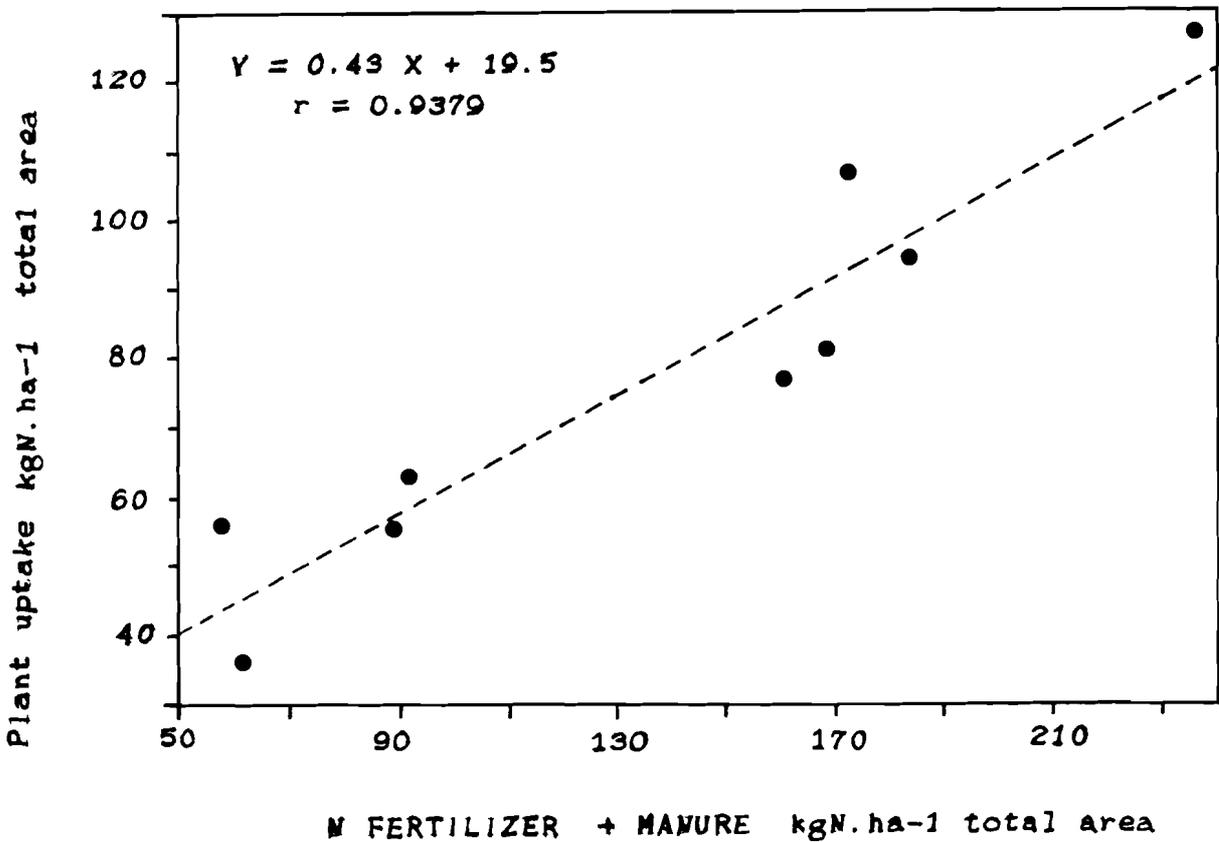


Figure 5 Plant uptake versus chemical fertilizer and manure application rates.

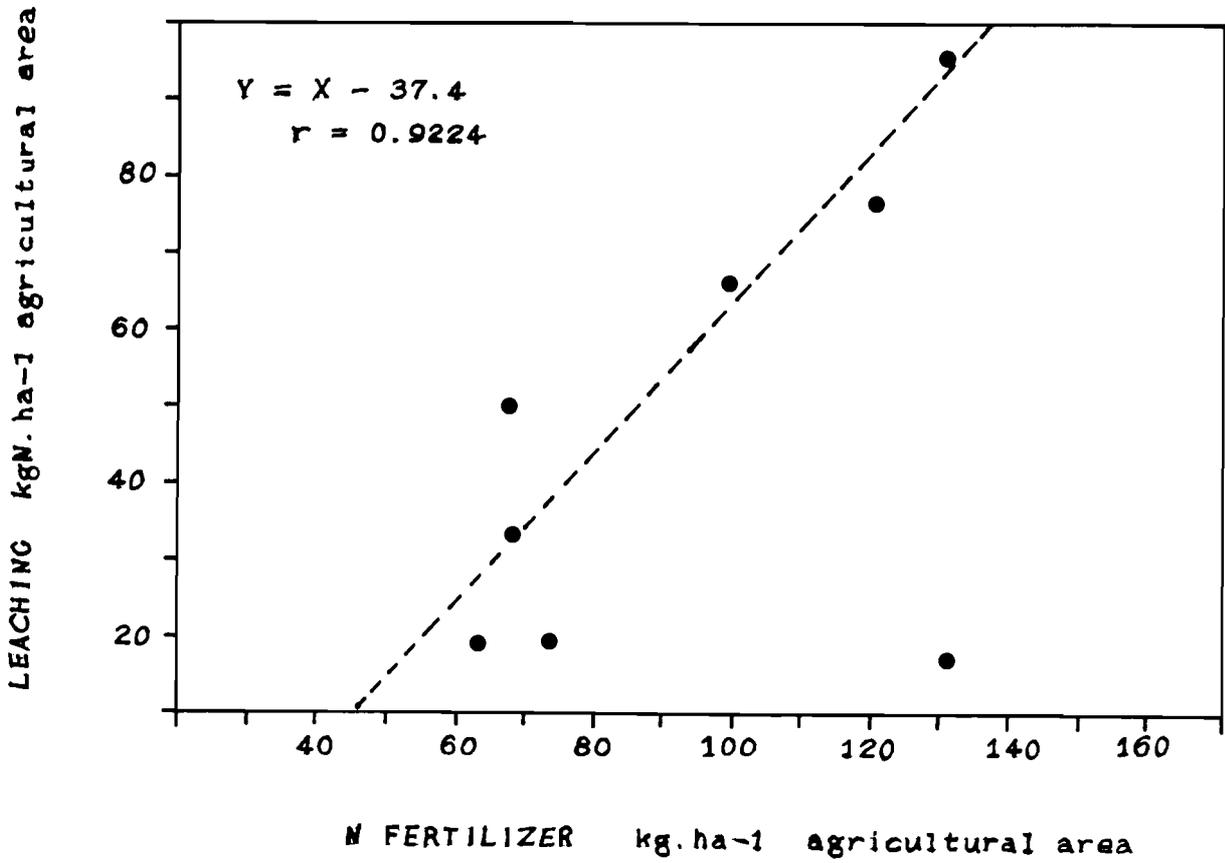


Figure 6 Leaching of nitrate versus chemical fertilizer application rates.

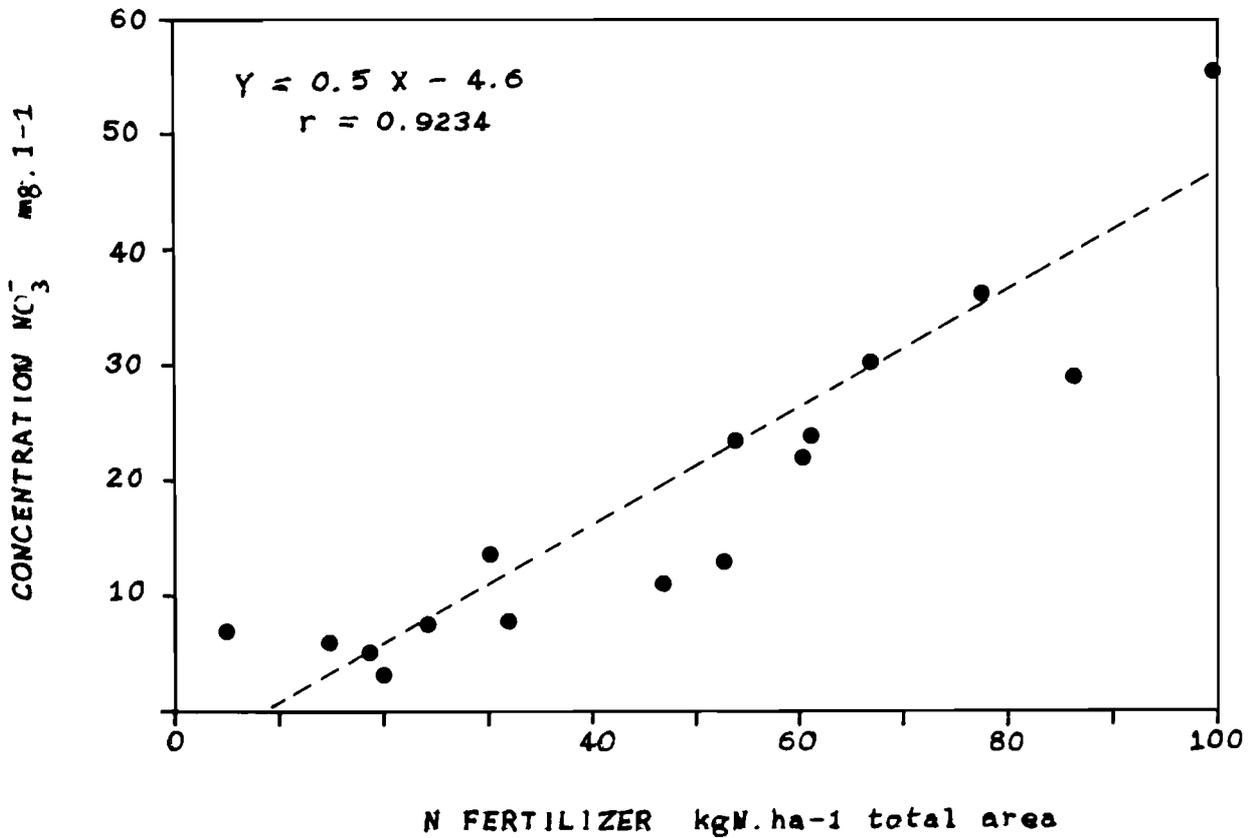


Figure 7 Nitrate concentration in river waters versus chemical fertilizer application rates.

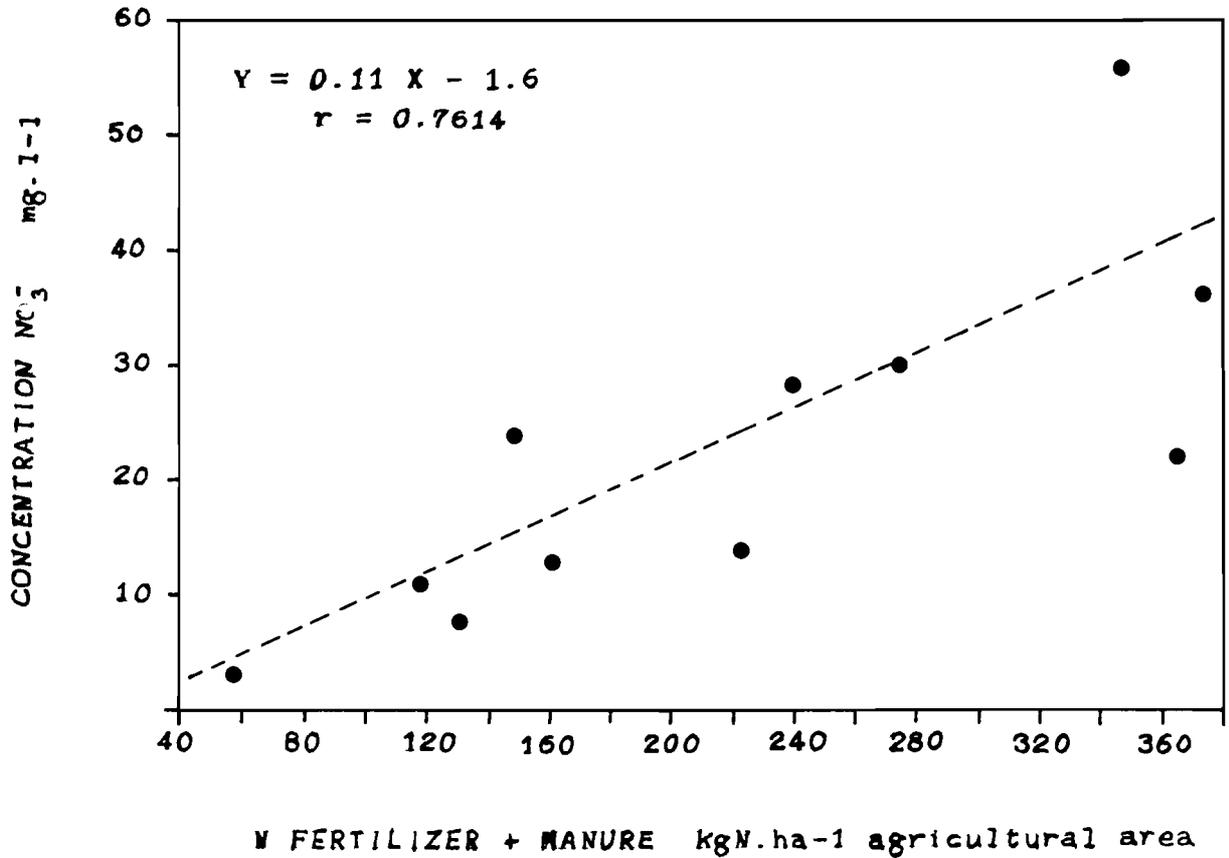


Figure 8 Nitrate concentration in river waters versus chemical fertilizer and manure application rates.

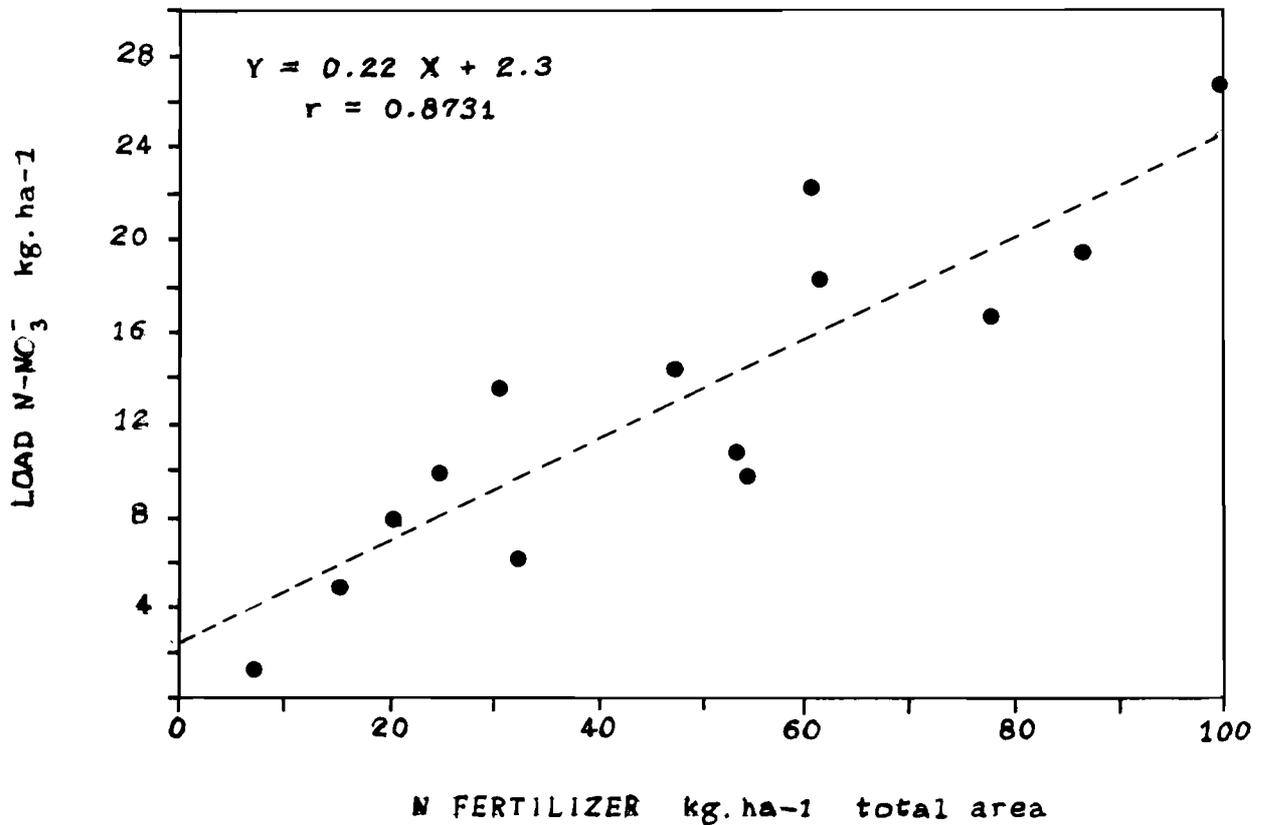


Figure 9 N-NO<sub>3</sub><sup>-</sup> exportation by rivers versus fertilizer application rates.

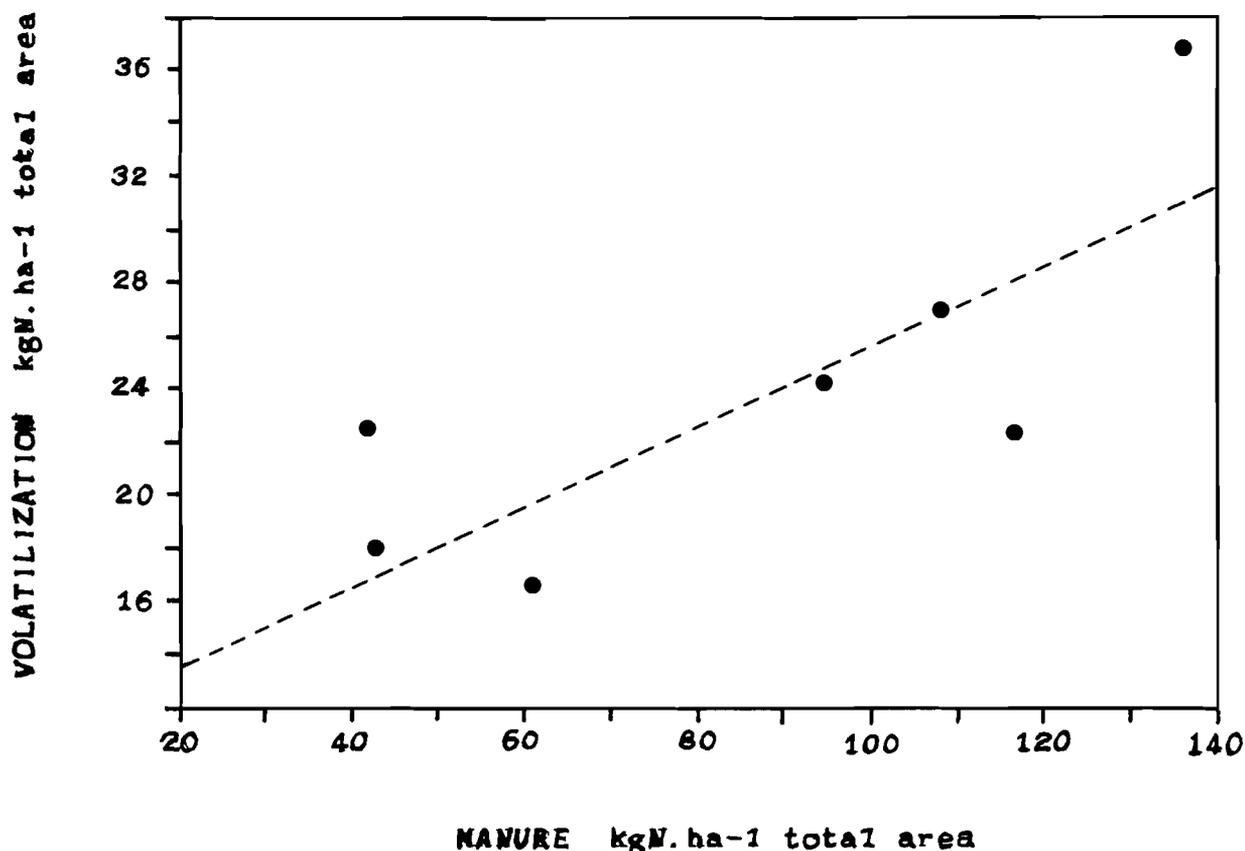


Figure 10 Volatilization of N-NH<sub>3</sub> versus manure application rates.

## 2.2. The Nitrate Problem in Groundwater and Surface Waters

### 2.2.1. Effects of nitrates on man

Nitrate as such is relatively non-toxic to human beings and animals, but under certain conditions it can be reduced to nitrite by denitrifying bacteria in the upper digestive tract of infants. Nitrates react with hemoglobin (methemoglobin formation) and reduce the capacity of blood to carry oxygen to the tissues. The symptoms vary according to the level of methemoglobinemia. Levels of 20 to 40% of methemoglobin in blood are generally accompanied by signs of hypoxia and symptoms such as weakness, external dyspnea, headaches, tachycardia and loss of consciousness. Death may occur at levels exceeding 50% of methemoglobin.

Possible development of cancer from nitrosamines may also result from the ingestion of water containing high concentrations of nitrate. It has been found that *Escherichia coli* and some species of streptococci could synthesize nitrosamines from nitrites.

### 2.2.2. Standards for nitrate in drinking water

Because of the lack of evidence of health problems occurring when nitrate concentrations in drinking water are below 50 mg NO<sub>3</sub><sup>-</sup> l<sup>-1</sup>, the standard adopted in 1980 by the E.E.C. was 50 mg NO<sub>3</sub><sup>-</sup> l<sup>-1</sup> for the maximum acceptable concentration, and 25 mg l<sup>-1</sup> for the recommended level. The nitrate limit for drinking water given by the World Health Organization (WHO) and the U.S. Environmental Protection Agency is 45 mg NO<sub>3</sub><sup>-</sup> l<sup>-1</sup>.

### 2.2.3. Utilization of groundwater and surface water in Europe

According to the Commission of the European Community (1982), 48% to 68% of the groundwater sources are used for drinking in western European countries (Table 6). The contribution of groundwater to the total used for the public supply varies according to the country (Table 7). Some countries like Denmark and the F.R.G. take most of their drinking water from groundwater, whereas some others like France, Ireland, and England, use much more surface water for the public supply. The population affected by the nitrate problem is therefore larger in countries using mainly groundwater, since groundwater is generally more enriched with nitrate than surface water owing to the denitrification process in the latter.

Table 6. Different uses of groundwater in Europe (in %).

	Drinking	Industry	Agriculture	Others	Total 10 <sup>6</sup> m <sup>3</sup>
BELGIUM	68	32 <sup>a</sup>			621
DENMARK	40	22	35	3	1317
FRANCE	55	32	8	5	5732
ITALY	53	12	34	1	12162
IRELAND	64	36 <sup>a</sup>			169
NETHERLANDS	61	34	5		1449
F.R.G.	48	49	2	1	7339

<sup>a</sup>) Indicates total for industry plus agriculture.

Table 7. Contribution of groundwater and river water to the total water used for public supply.

	GROUNDWATER	RIVER WATER
BELGIUM	67	33
DENMARK	95	5
ENGLAND	32	68
FRANCE	22	78
F.R.G.	90	10
IRELAND	23	77
LUXEMBOURG	45	55
NETHERLANDS	62	38

#### 2.2.4. Actual concentrations of nitrate in groundwater and river water

In France in 1980-1981, 80.4% of the population was supplied by water with less than 25 mg NO<sub>3</sub><sup>-</sup> l<sup>-1</sup>, 17.4% by water containing 25 to 50 mg NO<sub>3</sub><sup>-</sup> l<sup>-1</sup> and 2.2% by water with more than 50 mg NO<sub>3</sub><sup>-</sup> l<sup>-1</sup> (Ballay et al., 1985).

In the Great Ouse basin (England), 31% of sources for public water supply have nitrate concentrations below 25 mg l<sup>-1</sup>, 56% have concentrations between 25 and 50 mg l<sup>-1</sup>, and 13% exceed 50 mg l<sup>-1</sup> (Tester et al., 1985).

Nitrate concentrations in groundwaters often exceed 50 mg l<sup>-1</sup> in European agricultural areas, but some important variations occur according to the type of land use. For instance, in the Great Ouse basin, Tester, et al. (1985) found concentrations of 45 to 175 mg NO<sub>3</sub><sup>-</sup> l<sup>-1</sup> for fertilized arable land, 18 to 45 mg l<sup>-1</sup> for fertilized grassland, and 4 to 8 mg l<sup>-1</sup> for woodland and rough grazing. These values may be considered as representative of European groundwater and concentrations higher than 100 mg NO<sub>3</sub><sup>-</sup> l<sup>-1</sup> are now frequent in fertilized arable land. Since one half of the agricultural area is in arable land and the other half grassland, the actual concentration of nitrates in European groundwaters averages 45 mg l<sup>-1</sup>.

Nitrate concentrations are generally lower in river waters due to losses by denitrification in groundwaters and sediments as well as uptake of aquatic plants. These losses may be very important in rivers with long residence times and low specific discharges. They represent 9% of the upstream load in the river Meuse (Dermine, 1985), 33% in the downstream load (Billen et al., 1985 a,b), 30% in the Garonne River (Probst, 1983; Etchanchu 1987), and up to 73% in the Scheldt River (Billen, 1985a). Nitrate concentrations then generally decrease in the lower reaches of the largest European rivers and mean annual concentrations do not exceed 30 mg NO<sub>3</sub><sup>-</sup> l<sup>-1</sup> in most rivers (8 mg l<sup>-1</sup> in the Garonne and Moselle rivers, 14 mg l<sup>-1</sup> in the Meuse River, 16 mg l<sup>-1</sup> in the Rhine River). Nevertheless, we must stress the fact that nitrate concentrations display a marked seasonal variation.

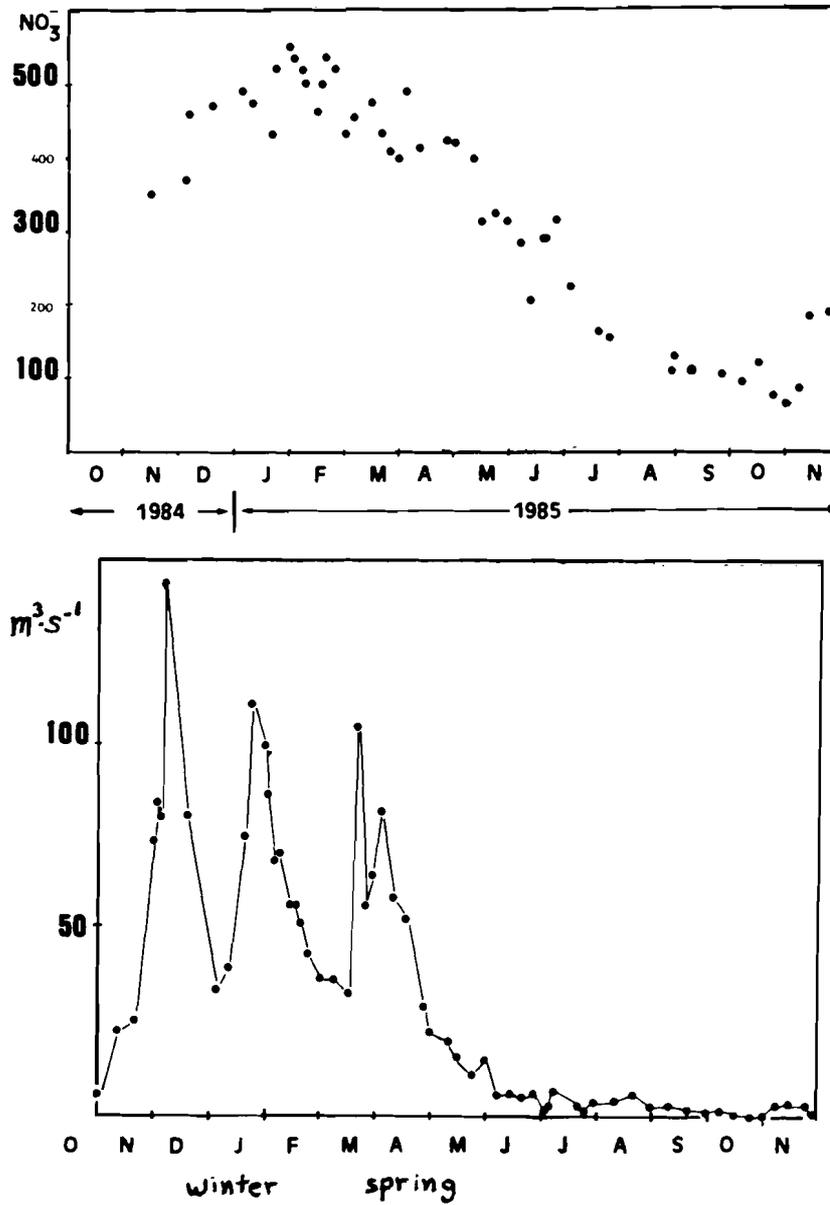
#### 2.2.5. Seasonality of the nitrate load in rivers

The seasonality of nitrate transport plays a dominant role in the quality of river water and in the ecological disequilibria in coastal waters. Peak periods of nitrate concentration occur simultaneously, in most cases, with peak periods of water discharge (Figure 11).

A typical logarithmic relationship can be found between nitrate concentration and water discharge (Belamie, 1983; Dermine, 1985; Souchu, 1986 a,b; Etchanchu and Probst, 1986). (See Figure 12). Such a relationship characterizes a non-point source pollution where soil leaching is predominant.

During highflow periods nitrate concentrations may sometimes reach the E.E.C. limit, but during storm runoff events, the concentration decreases by dilution when surface runoff occurs and becomes dominant.

Consequently, in many rivers, more than 90% of the annual load of nitrogen is transported into marine ecosystems during the winter period (between November and April) when biological processes are slowed by climatic factors and longer residence times (Figure 13). On the other hand, domestic and industrial inputs represent the main sources of nitrogen to the rivers during the summer period. Their contribution to the annual load is variable according to the country, 20% Denmark (Hagebro et al., 1983), 40% in Finland (Kauppi, 1984), and 65% in Belgium (Billen et al., 1985 a,b).



*Figure 11* Comparison between the fluctuations of nitrate concentrations and the water discharge in the Aulne river (Brittany) (Souchu, 1986 a,b).

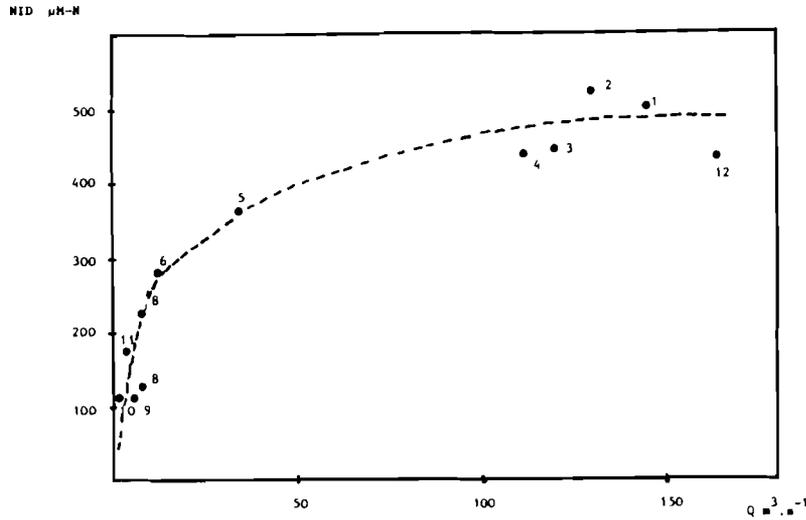


Figure 12 Relationship between the nitrate concentrations measured in the Aulne river and the water discharge (Souchu, 1986 a,b).

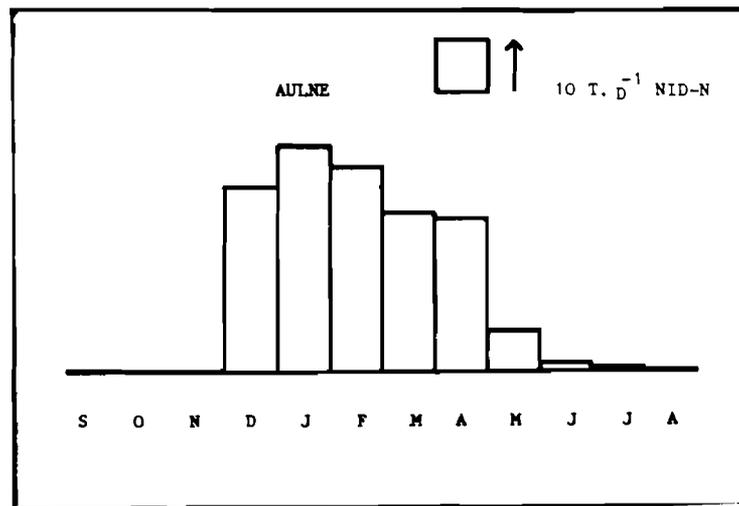


Figure 13 Monthly transport of dissolved inorganic nitrogen by the Aulne river (10 tons per day) (Souchu, 1986 a,b).

### 2.2.6. Eutrophication problem

The nitrogen and phosphorus added by agricultural leaching and waste water effluents contribute significantly to the eutrophication process, which can be considered as a major problem in many lakes. The amounts of inorganic nutrients available is usually the limiting factor to autotrophic growth, but in some cases the amount of light may also be the limiting factor because of high turbidity levels in the water. Although the eutrophication problem is less severe in river waters because of shorter residence times, attention can be drawn to some possible consequences of using eutrophic water for water supply and other purposes. Among problems resulting from this ecological disequilibrium, clogging of water treatment filters, undesirable taste and odor can be mentioned.

### 2.3. Estuaries

#### 2.3.1. Introduction

Estuaries are some of the most thoroughly studied ecosystems since they form the boundary for mixing between fresh and sea waters. Also, they are characterized by complex biological, chemical and physical processes in which nitrogenous compounds are involved. It is beyond the scope of this paper to investigate the many diverse functions of nitrogenous compounds in estuarine processes. Rather, we focus on the fate of nitrogen of agricultural origin, and the role played by industrial and domestic sewage in estuarine waters.

#### 2.3.2. Winter period

Rivers transport nitrogen (in nitrate form) to estuaries during the highflow period, and most of the nitrogen in river waters originates from leaching for agricultural land. In winter and spring, the behavior of nitrogen is controlled by physical, chemical and biological processes (Wollast and Duinker, 1982). The main biological processes incorporate nitrogen into organic compounds. Nitrogen is released by the mineralization of particulate and dissolved organic matter through denitrification and other microbial processes (Zwolsman, 1986). One of the best ways of estimating the behavior of nitrate in estuaries is to compare the changes in its concentration with changes in chlorinity (or salinity, S) along the salinity gradient. A theoretical dilution line can be drawn between the riverine concentration (S=0‰) and the concentration found in sea water (S=35‰). As we have seen, concentrations in river water exhibit much seasonal variation (Figure 11). Most important is the winter rainy season since more than 90% of the nitrogen is discharged to coastal ecosystems during this period (Figure 13). In the Aulne and Elorn estuaries, dissolved inorganic nitrogen concentrations strongly follow the theoretical dilution curve and consequently display a conservative behavior during winter months (Figure 14). This general pattern can be extended to the majority of European estuaries. During flood periods, the short residence time of estuarine waters as well as the climatic conditions (low temperature and little light) strongly limit biological processes. Consequently, nitrate-enriched freshwaters are quickly dispersed into coastal waters due to the action of tidal currents and the river-flushing effect. Only the establishment of frontal zones following the flood period prevents the dilution of nitrate-rich freshwaters with oceanic waters.

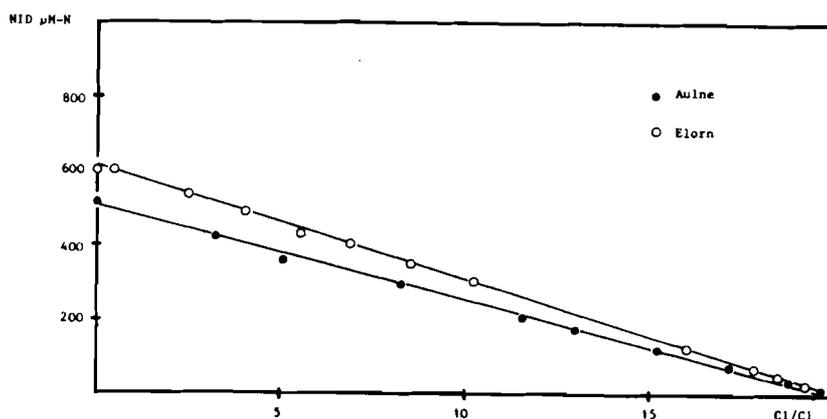


Figure 14 Conservation of dissolved inorganic nitrogen in Aulne and Elorn estuaries in winter as a function of the theoretical saline dilution curves.

### 2.3.3. Summer period

In temperate ecosystems, the low water levels and long residence times associated with the summer period promote not only stratification in the estuary, but also biological processes. These conditions foster non-conservative behavior of many dissolved chemicals, especially nitrogenous compounds, along the salinity gradient. With decreasing rainfall accompanied by decreased leaching of soils, nitrogen inputs from agricultural lands decrease, but domestic and industrial inputs remain the same. Although precise quantitative data are lacking, the available evidence suggests that sewage can constitute an important source of nutrients (about 20% of the total amount in Europe) in coastal waters that are frequently nitrogen-depleted during summer (Souchu, 1986 a,b). The non-conservative behavior of mineral nitrogen suggests that it is partially removed within the estuary by phytoplanktonic uptake and bacterial processes. The Scheldt estuary (Belgium) is a good example (Wollast and Peters, 1978; Billen et al., 1985 a,b): 80% of nitrogenous compounds entering the estuary is of domestic and industrial origin. The long residence time of water characterizing this estuary (30 to 90 days) promotes intensive mineralization of organic compounds and therefore depletion of dissolved oxygen. Since nitrate serves as an oxygen source, two-thirds of the nitrogen amount discharged to the estuary is removed, chiefly by denitrification (Figure 15).

However, the anoxic conditions prevailing in the estuarine waters of the Scheldt may not be representative of all European estuaries. Nevertheless, this example focuses on the potential importance of estuaries as sinks for nitrogenous compounds under heavy organic-matter loading conditions. Additionally, phytoplanktonic species (essentially diatoms) contribute to the consumption of the total dissolved inorganic nitrogen during this period.

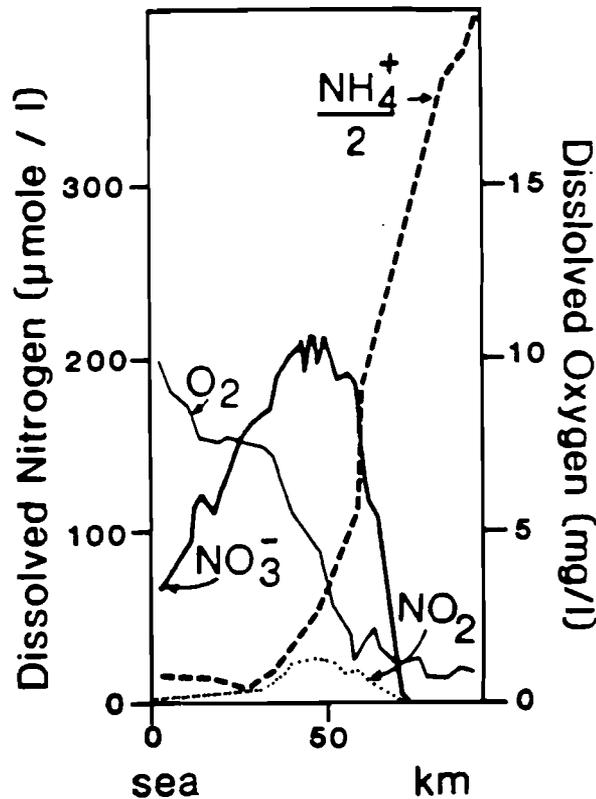


Figure 15 Longitudinal profiles of dissolved nitrogen species and oxygen in the Scheldt estuary during the summer (from Wollast, 1983).

#### **2.3.4. Conclusion**

In the absence of climatic anomalies (e.g., dry winter or rainy summer), a general pattern can be described to understand the response of estuaries to nitrogen inputs of anthropogenic origin:

- 1) During flood periods (generally between November and April), estuaries simply act as corridors for nitrogen of agricultural origin (nitrate lost from soil leaching). In winter, this source contributes more than 90% of all nitrogen inputs to the aquatic ecosystems.
- 2) During dry periods, inputs are very small and stem primarily from industrial and domestic sewage. Biological processes, especially denitrification and consumption by phytoplankton which are enhanced by the increase of temperature and residence time of waters, consume much of the nitrate before it reaches the estuary.

## **2.4. Coastal Waters**

### **2.4.1. Availability of nutrients in relation to phytoplankton dynamics**

During winter, temperature and light play the major role in limiting plant production, but in spring nutrients rapidly become the most important limiting factor. Rivers constitute an important pathway of fertilization for marine ecosystems and primary productivity may respond to high nitrogen inputs by increased production rates. In addition, dissolved silica may limit diatom and silicoflagellate growth. Phosphorus is also important in controlling macro- and microphyte growth.

In the North Sea, the inputs of nitrogen have been estimated at 1.5 million tons per year, and those of phosphorus at 0.1 million tons (International North-Sea Conference, 1987): that gives an N/P ratio of 15 which is very close to the Redfield's ratio. Considering the faster recycling of phosphorus and potential inputs of phosphorus from sediments, it is justified to stress the role of nitrogen inputs in assessing eutrophication problems. In contrast to nitrogen and phosphorus, anthropogenic sources of dissolved silica are unimportant compared to natural weathering reactions (Zwolsman, 1986). Consequently, excessive nitrogen in coastal water may promote species which do not consume silicon. The question of limiting factors is very complex, and even if we commonly assume that nitrogen is the main factor limiting primary productivity in marine water, there are always exceptions (Martin-Jezequel, 1981; Queguiner, 1986). For example, Hafsaoui, et al., (1985) have shown that, in the Bay of Brest (typical coastal ecosystem in the western part of France), each nutrient (N and Si alone, P + Si, and N + Si at the same time) can limit the pelagic primary production depending on season and depth.

At the beginning of the growing season, diatoms dominate the phytoplankton population leading to nutrient-depleted conditions. During the following period, oligotrophic conditions occur and the dominant species are commonly dinoflagellates (Margalef, 1984), which, as explained in the next section, sometimes cause serious ecological problems. The coastal waters are one of the most vulnerable areas in the marine ecosystem since they are directly exposed to terrestrial inputs. Thus the response of macrophytes to increasing concentrations of nitrogen in near-shore waters is of critical importance.

### **2.4.2. Coastal eutrophication and "red tides"**

#### **2.4.2.1. Introduction**

Red tides have been documented throughout history in all parts of the world. The occurrence of a dense population of a single phytoplankton species is not in itself striking. However, some outbreaks of toxic dinoflagellate species lead to mass killings of marine invertebrates and fish, and to "shellfish poisoning". Humans eating contaminated shellfish may also be poisoned. The frequent occurrence of such phenomena since the 1960's and their economic impact have caught scientists' attention (Partensky and Sourina, 1986). Among marine phytoplankton, dinoflagellates form a large family whose taxonomy and complex variation of toxic effects give rise to much discussion. (For example, see Reid, 1980.)

#### **2.4.2.2. Biological and physiological characteristics of dinoflagellates with emphasis on *Gyrodinium aureolum***

##### ***Tolerance to physical factors***

Although dinoflagellates have been observed in waters displaying a large temperature range, the blooms of these species are more frequently recorded in warm water (15° to 20° C), and are usually absent from waters with temperatures under 10° C. On the

other hand, they show euryhaline (0 to 36%) and euryphotic properties.

#### *Chemical demand*

Dinoflagellates differ from diatoms in that they do not need silica for their growth. So, from a nutritional point of view, their productivity only depends on the availability of nitrogen and phosphorus compounds. They are less sensitive than the diatoms to chemical pollutants such as hydrocarbons, and their growth can be enhanced by polluted waters (Greve and Parsons, 1977). *Gyrodinium aureolum* is capable of assimilating dissolved inorganic nitrogen in the dark. Queguiner (1986) has pointed out that some species can consume organic phosphorus. But most importantly, they have flagella and are thus able to swim downward into the nutrient-rich deep water to obtain nutrients during the night and return to the euphotic zone during the day (Cullen and Horrigan, 1981).

#### **2.4.2.3. Occurrence of red tides and their dependence on anthropogenic nutrient sources**

The hypothesis of Legendre and Demers (1985) states that phytoplanktonic blooms always occur at the spatio-temporal interface between unstable and stable conditions. Spatio-temporal interfaces include thermoclines, haloclines and stabilization-destabilization rhythms in the water column (spring tide-neap tide, flow ebb). All these interfaces can be described by the global term of "ergocline". The concept of ergocline is illustrated in the literature with regard to the occurrence of red tides. It is well known that stratification of water is favorable and even necessary to dinoflagellate blooms (Guzman and Campodonico, 1978; Fonda Umani, 1985; Garcon et. al., 1986).

In Northern European marine waters, the geographic distribution of red tides is closely linked with frontal zones which are established outside some coastal areas between April and September. (See Figure 16.) As indicated earlier, most of nitrogen of agricultural origin is discharged into the continental shelf waters during flood periods. In many cases, these nitrogen enriched waters are prevented from dilution with oceanic water by the establishment of frontal zones. This may constitute an important method of nutrient enrichment required for dinoflagellate blooms occurring in this zone (Figure 17).

Storms and heavy rainfalls can be followed by red tides in coastal waters (Morton and Twentyman, 1971; Schrey, et. al., 1984). Such storms mix nutrient-rich deep water with the surface layer. The subsequent return to stable conditions (warming of surface water and absence of wind) provides a temporal physico-chemical transition which can promote dinoflagellate blooms.

Rainfall itself is also a potential source of nutrients for phytoplankton (Correll and Ford, 1982; Duce, 1985; Paerl, 1985). Volatilization of ammonia from manure and emission of  $\text{NO}_x$  from industrial activities contribute to atmospheric sources of nitrogenous compounds. Heavy rainfalls (as may occur during summer) can lead to the deposition of a several millimeter-thick layer of nitrogen-enriched freshwater onto the marine surface water. Under optimum conditions of stability (neap-tide, absence of wind), the mixing of rainwater with marine water is limited to the upper few centimeters and the halocline may enhance dinoflagellate blooms.

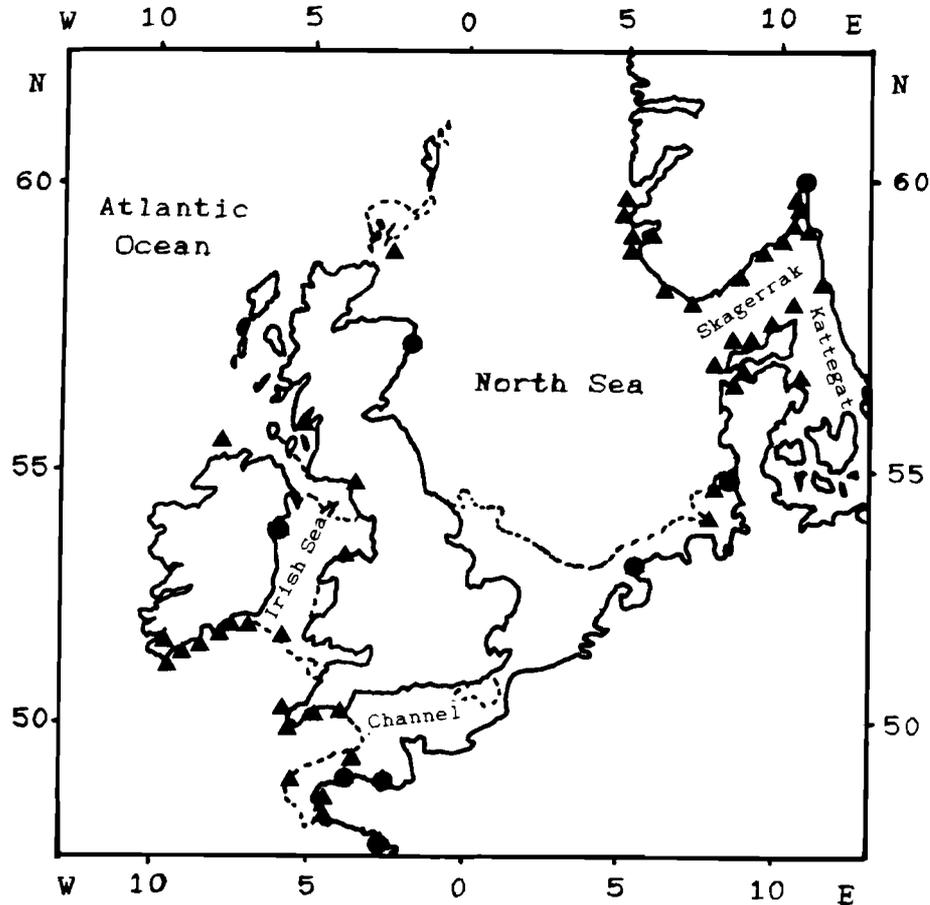
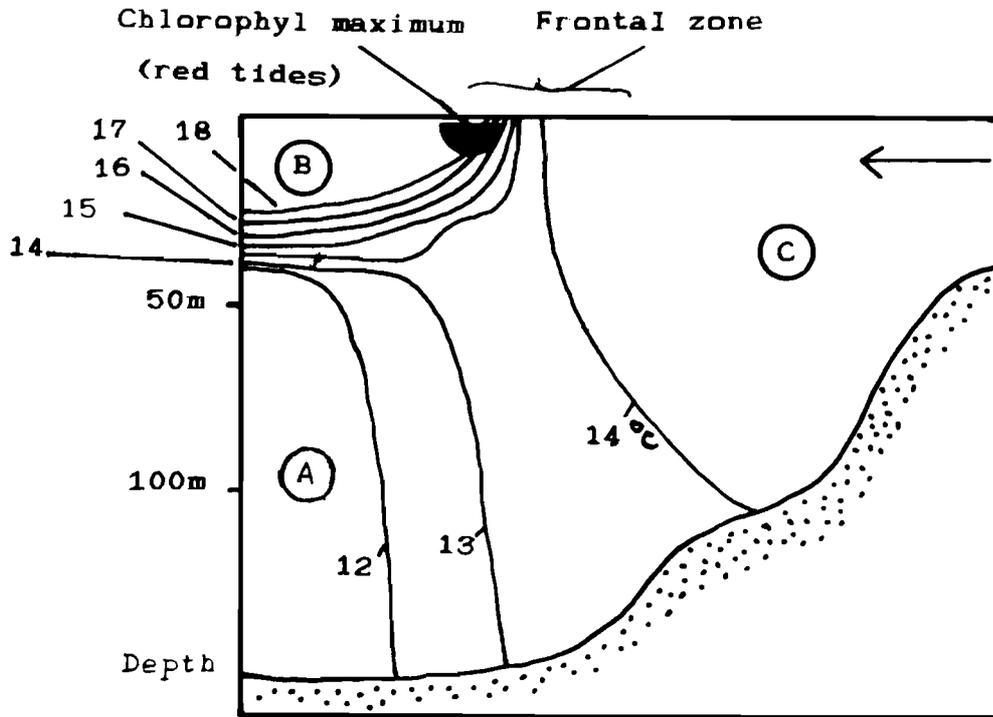


Figure 16 Distribution of red tides (▲, *Gyrodinium aureolum*) in North European waters (after Partensky and Sourina, 1986) and of green tides (●) (after Brault et al., 1986).

#### 2.4.2.4. Economic and ecological consequences of red tides

Toxic effects of dinoflagellates on other marine organisms are well documented (e.g. see review by Partensky and Sourina for *Gyrodinium aureolum*, 1986). Invertebrate species (lugworms, sea-urchins, molluscs, etc.) as well as vertebrate species are affected. When flagellates are the main source of food for zooplankton, the food web pathway tends to favor marine predators of no economic interest, such as stenophores or medusae (Greve and Parsons, 1977). On the other hand, diatom species usually support a food web pathway favoring young fish of economic interest. Moreover, dinoflagellates more easily deplete waters of oxygen than do diatoms because of the high mucilage concentration associated with their blooms. The mucilage increases the viscosity of surface waters and consequently hinders efficient oxygenation of deeper layers, especially in stratified waters. Toxins released by many dinoflagellate species render shellfish unsuitable for human consumption, and their toxic effects on other marine species cause serious problems for the aquaculture industry.



**Figure 17** Typical distribution of temperature for frontal zones in European coastal waters. They develop in spring and disappear in fall. Three water-masses can be characterized: (A) Oceanic water under the thermocline and the aphotic zone, cold and not nutrient-depleted; (B) oceanic water above the thermocline and in the aphotic zone, warm and nutrient-depleted; (C) coastal water well-mixed by tidal current, nutrient-enriched by freshwater. Provides nutrients for phytoplanktonic blooms taking place at the frontal zone.

### 2.4.3. Coastal eutrophication and "green tides"

#### 2.4.3.1. Introduction

Excessive growth of green seaweed, called "green tides", in Brittany (France), is becoming a common phenomenon in sheltered marine bays (see Figure 16.) The algal species involved in the development of green tides belong chiefly to the family of Ulvaceae, whose main genera are *Enteromorpha* and *Ulva*. These algae are inclined to proliferate in shallow bays with low wave conditions and absence of wind. They start blooming at the beginning of the summer period and form thick algal mats (10 to 15 cm) on the shoreline where they remain until the first autumn storms and equinox tides remove them. This mode of eutrophication is attributed to the increasing discharge of nitrate from agricultural runoff to coastal ecosystems, but sewage effluents also contribute to the problem.

#### 2.4.3.2. Ecology and resilience of Ulvaceae

##### *Tolerance to physical factors*

The successful growth of these plant species is governed by several physical factors (Fitzgerald, 1978; Lowthion, et. al., 1985). Numerous species of *Ulvaceae* are known to tolerate drastic changes in salinity (0 to 40%) owing to their osmoregulatory system which is capable of accumulating salts against a diffusion gradient. Their eurythermal properties are evident from the wide distribution of these algae in both tropical and temperate waters. Since *Ulva* and *Enteromorpha* species have no mucilaginous covering, they are likely to die quickly upon dessication, but the thickness of the mats reduces evaporation, thus ensuring a favorable microclimate for the subsurface macroalgae. Finally, these algae have a wide tolerance to varying light intensities.

##### *Chemical demands*

Green algae display a wide tolerance to polluted waters (Edward, 1972), and they respond vigorously in culture to enrichment by sewage effluent (Montgomery et. al., 1985). Harlin and Thorne-Miller (1981) have shown that ammonium and nitrate enrichment strongly stimulate the growth of green algae in seagrass beds (while a red one, *Gracilaria tikvahiae* was not enhanced). Phosphate has no effect, doubtlessly because of the availability of this nutrient due to release from sediments (Montgomery, et. al., 1985). *Ulva* sp. is capable of incorporating at the same time both ammonium and nitrate. It can maintain a reduced growth rate during long periods (up to 44 days) under limiting nitrogen conditions and can also absorb organic nitrogen as urea (Brault, et. al., 1986). Consequently, *Enteromorpha* and *Ulva* species are virtual nitrogen sponges and it is not surprising that in seagrass beds they compete successfully, grow rapidly, and shade other benthic plants. It is quite obvious that a spill of nutrients (especially nitrogen) into semi-enclosed shallow marine systems may promote blooms of green seaweeds.

#### 2.4.3.3. Ecological and economic consequences of green tides

##### *Ecological consequences*

Along the western European shore, wide areas of former open mudlands are covered by proliferating green algae during the summer period. The effects on the underlying sediment have repercussions on the entire food web. First, the thickness of the mats prevents the sediments from becoming oxygenated, which may lead to anoxia with hydrogen sulfide release (Warfe, 1977; Nicholls, et. al., 1981). Moreover, algal mats contribute to accumulation of organic particles in the sediment (Frostick and McCave, 1979). Dense algal mats on the surface sediments change the invertebrate macrofauna beneath them, first by reducing the biomass and the diversity of the mud-dwelling infauna (Warfe, 1977; Reise, 1983), but also by increasing the number of epibenthic animals, especially grazing species (Nicholls et. al., 1981). The infauna of intertidal flats supports large populations of fish and bird predators. Since the proliferation of green algae promotes herbivorous species (ducks and geese), the physical presence of the mats themselves prevents other birds, such as waders, from exploiting the fauna under and within the mats (Soulby, et. al., 1982).

##### *Economic effects*

Green tides are viewed as a nuisance by the hotel and tourism industries since the algae accumulate on recreational beaches. If algal mats are not removed and the beaches raked frequently, they hinder bathing and boating. Moreover, there are episodes of obnoxious odors attributable to the algal decay. Green tides may be considered as an important source of pollution since they can lead to anoxia and release of hydrogen sulfide. The

latter is highly toxic for shellfish beds (cockles, mussels) which are exploited by fisheries.

#### 2.4.4. Conclusion

Dinoflagellates and green algae display a wide adaptability to drastic changes in physico-chemical conditions in the environment (temperature, salinity, light and nutrient levels). They are more able than other species to grow in polluted waters and therefore can take advantage of nutrient inputs of anthropogenic origin. Red tides more often occur in frontal zones where they find optimum conditions of growth, and the enrichment of coastal waters by nitrogen of agricultural origin may be a determining factor in this eutrophication process. It must be stressed that especially nitrogen-enriched rainfalls (with ammonia from manure volatilization for instance) provide favorable conditions for dinoflagellate blooms. Though the development of green tides is limited to sheltered bays, their growth area corresponds to the richest biological near-shore zones (oyster and mussels beds) and also to recreational beaches.

Increasing nitrogen (and also phosphorus) levels may be expected to produce changes in these algal populations in the future. Their increase could lead to large areas of shoreline becoming unsanitary and even poisoned, owing to the decay of the algae and release of hydrogen sulfide under anoxic conditions prevalent in the underlying sediment. The resulting disappearance of numerous invertebrate and vertebrate species could constitute a chief ecological disequilibrium for near-shore ecosystems. Though economic consequences resulting from green tides may be disastrous for shellfisheries, the consequences of the increasing dominance of dinoflagellates in the food-web are even more serious. In addition to the direct toxic effects caused by red tides, dinoflagellates do not constitute an available food source for the trophic chain leading to small fish. Hence, in areas dominated by dinoflagellates, economically important fish species may become extinct.

### 3. CHANGES IN THE PAST

#### 3.1. Structural Changes

##### 3.1.1. Before the Agricultural Revolution (several millenia ago)

Before the Agricultural Revolution, most European soils were covered by forest. In this ecosystem, the nitrogen cycle displayed a simple pattern (Figure 18) and the different nitrogenous compounds (inorganic and organic nitrogen) were efficiently utilized. Thus losses from soils were very small.

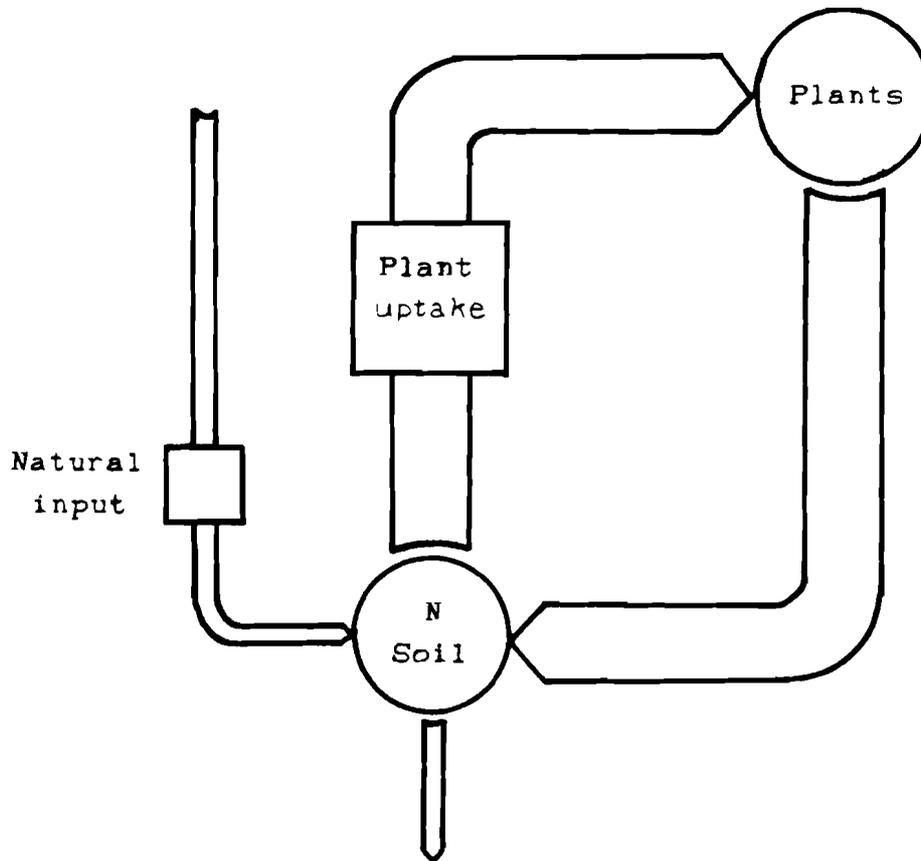


Figure 18 Nitrogen cycle in a forest ecosystem (after Billen et al., 1983).

##### 3.1.2. The Agricultural Revolution (more than 300 years ago)

During the Agricultural Revolution, agricultural areas were more or less closed systems where the minor export of products and the efficient utilization of manure as a fertilizer avoided major losses of nitrogen (Figure 19). Fallow and leguminous cultivation were practiced to maintain good soil fertility. Agricultural yields were also relatively low.

##### 3.1.3. The Industrial Revolution (the last 300 years)

During the Industrial Revolution, the development of "urban societies" and the increasing demand for agricultural products led to structural changes in agriculture (Figure 20). Replacing the closed system was one where large amounts of food and fodder were exported to the cities and intensive livestock-breeding areas. In order to increase the productivity of agriculture and to compensate for the nutrient export, more land had to come under cultivation. After World War II, increasing demand was met by adding ever increasing amounts of synthetic nitrogen fertilizer per unit of land area. With regard to the nitrogen cycle, the nutrients consumed by urban dwellers do not return to the soil, but are directly discharged to sewage systems and subsequently into the aquatic environment.

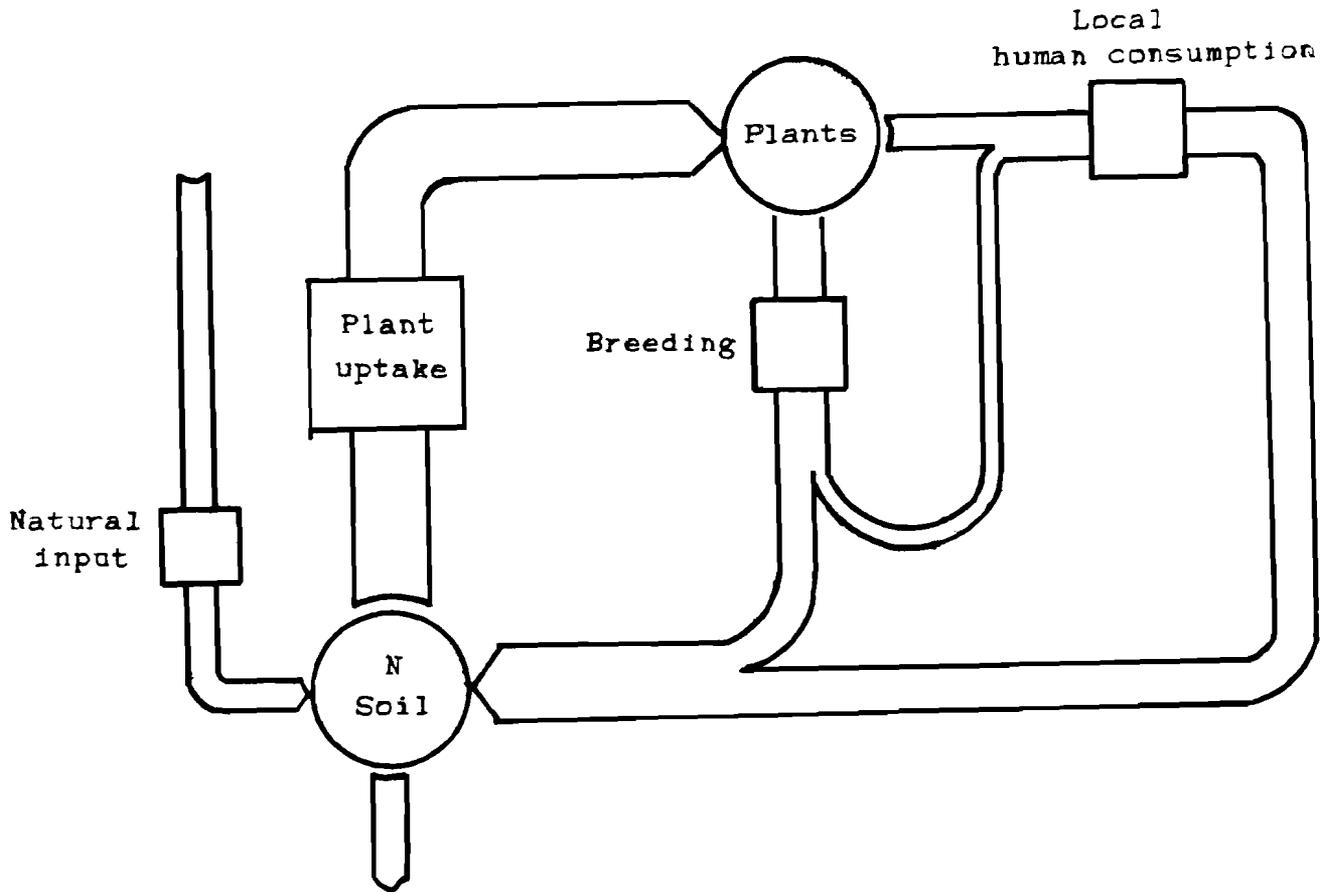


Figure 19 Nitrogen cycle in a traditional agriculture system before Industrial Revolution (after Billen et al., 1983).

Moreover, the latter receives nitrogen due to leaching of excess chemical fertilizers from the soil. This basic system has remained unchanged for the last 40 years, except that the losses of nitrogen to aquatic environments have increased owing to enhanced agricultural activities and urban growth. (Compare Figures 20 and 21.)

### 3.2. Trends of Agricultural Inputs and Outputs Between 1958 and 1984

Although the amount of arable land in Europe has decreased by 8% during the period 1958-1984 (Eurostat, 1985), application of chemical fertilizer increased 3.5-fold during that period (Figure 22). Intensification of breeding activities has increased the amount of manure 1.3-fold, but it is not completely returned to the soil; about 20% is dumped into the aquatic environment. The "natural input" to the soil decreased 1.3-fold, even though the load of nitrogenous compounds in atmospheric precipitation increased. The decrease was mostly due to the decline of leguminous plant cultivation by 12% (Eurostat, 1985). At the same time, plant uptake of nitrogen increased only 1.5-fold (Figure 23). Thus, one may assume that the rate of leaching has tripled.

In conclusion, the agricultural system has continuously increased its losses to the aquatic environment, mostly by leaching of nitrate-nitrogen from the soil. Moreover, manure has become a pollutant rather than a resource as it once was, and the increase of domestic and industrial sewage (1.7-fold) has contributed to the added inputs of nitrogen to aqueous systems.

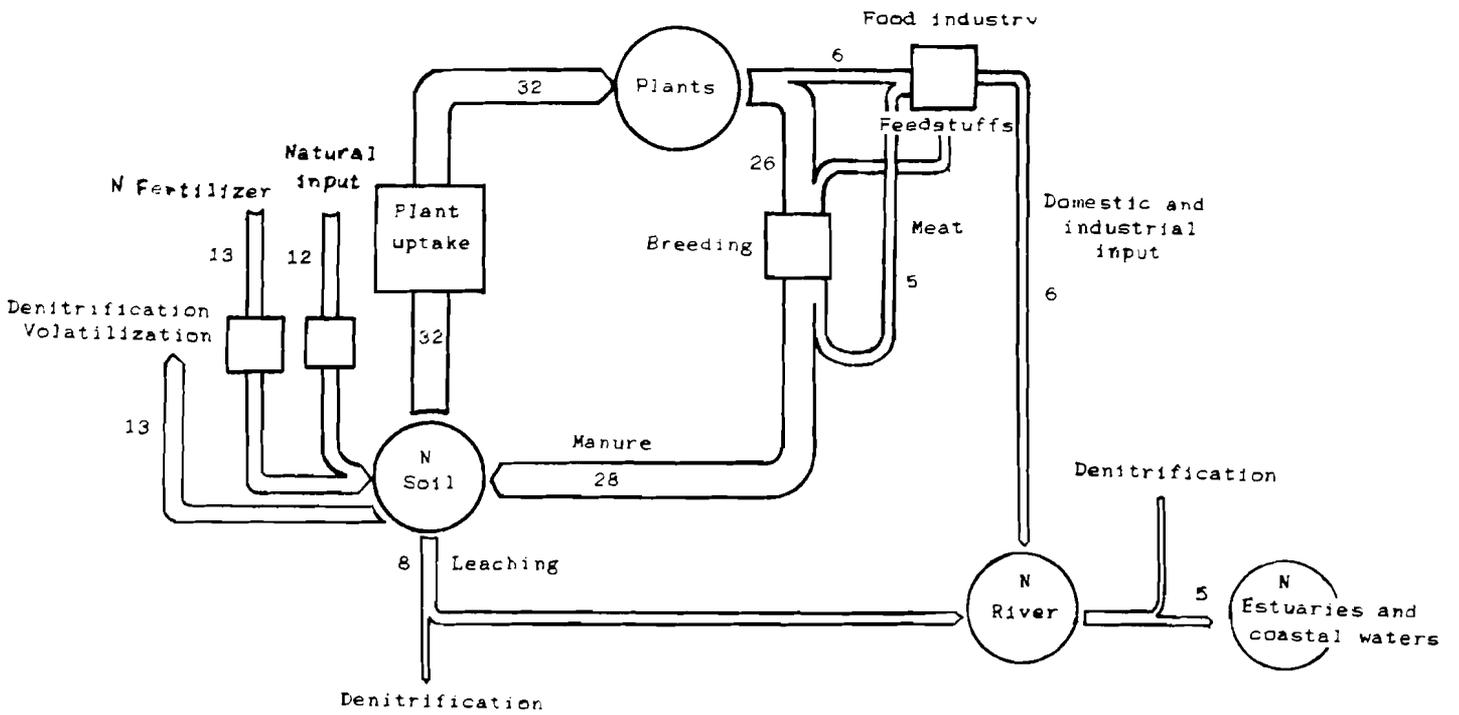


Figure 20 Nitrogen cycle in Europe in 1958, in  $\text{kg ha}^{-1} \text{yr}^{-1}$  (of total area).

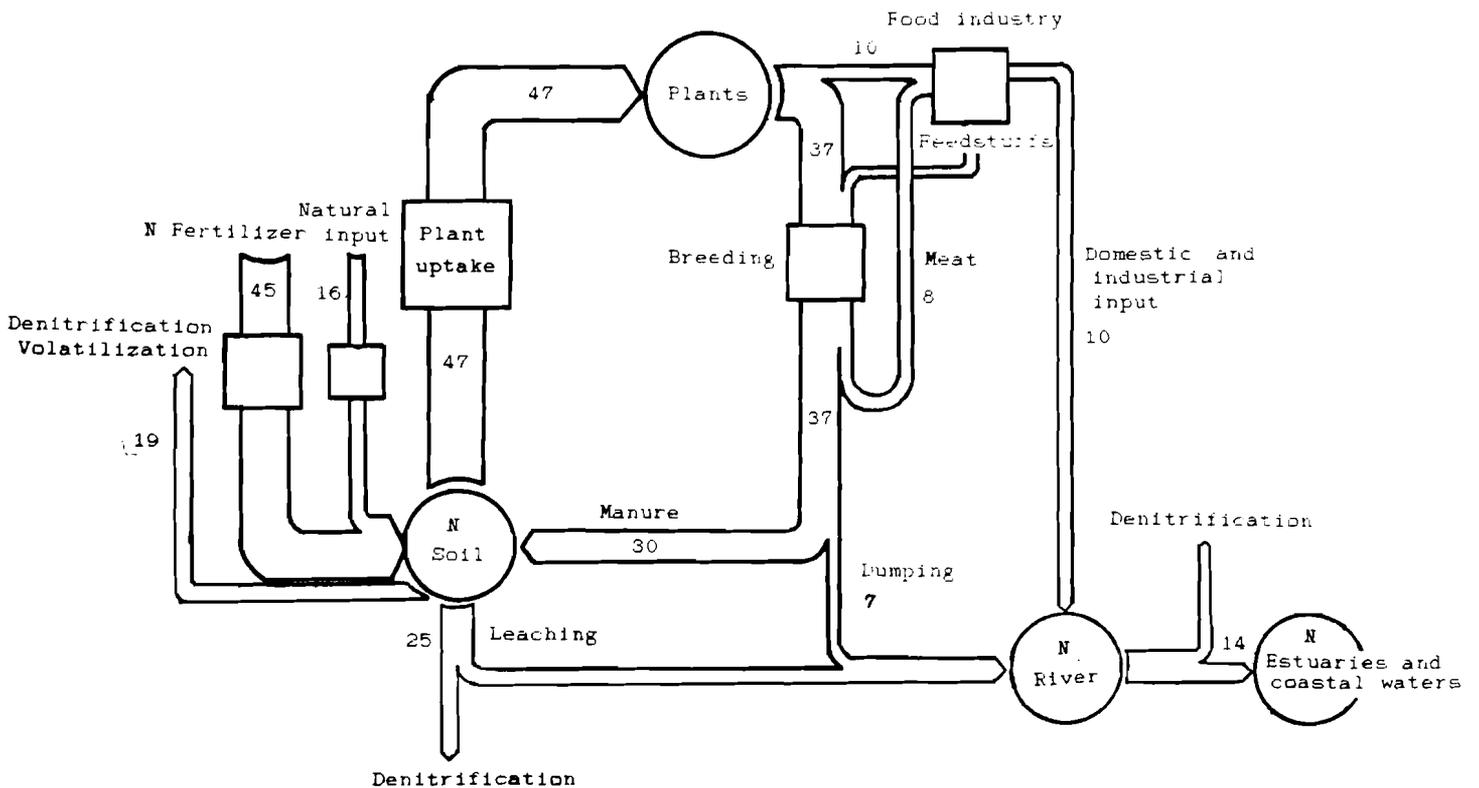


Figure 21 Nitrogen cycle in Europe in 1984, in  $\text{kg ha}^{-1} \text{yr}^{-1}$  (of total area).

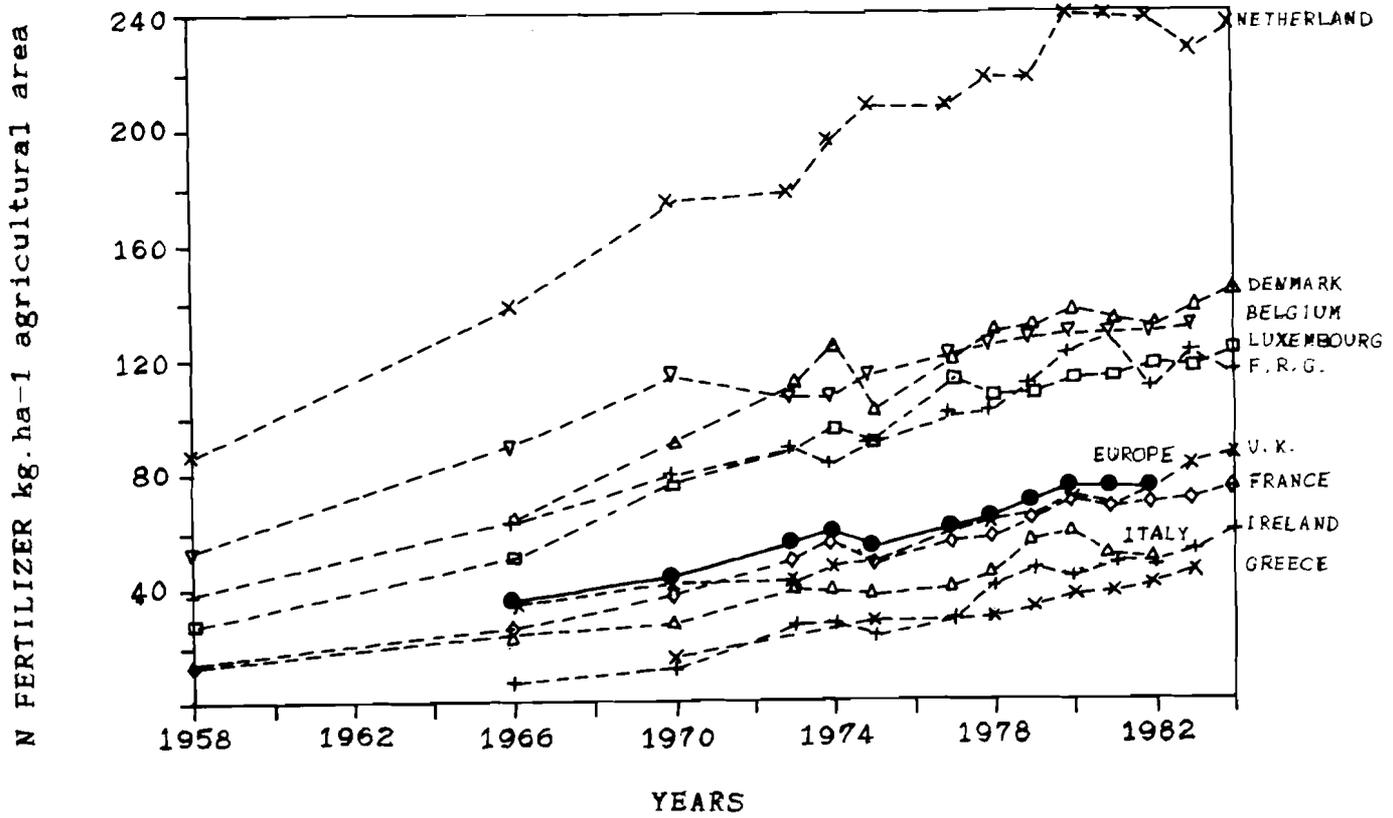


Figure 22 Trends of fertilizer application in European countries between 1958 and 1984.

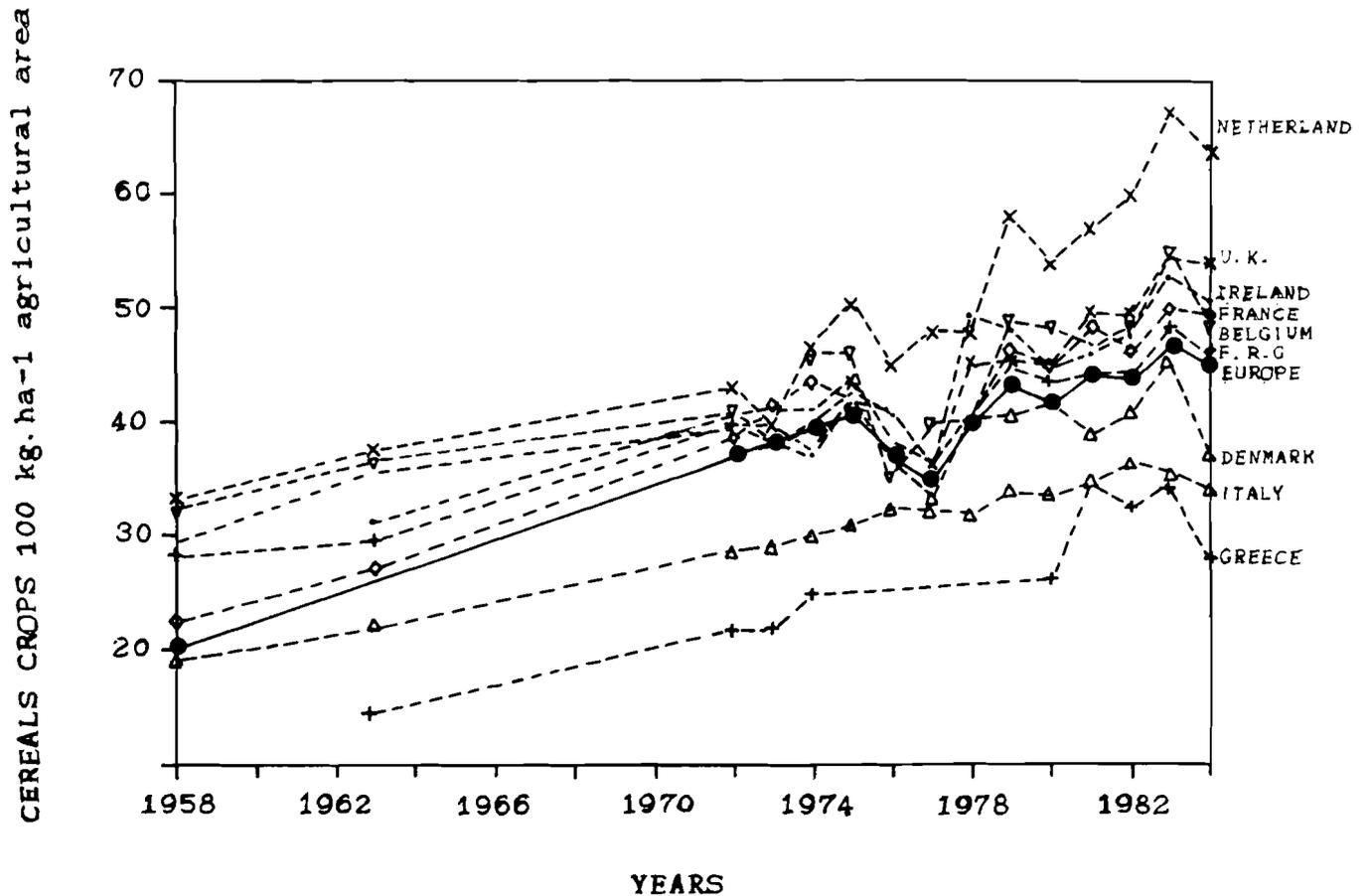


Figure 23 Trends in cereal cropping in European countries between 1958 and 1984.

### **3.3. Environmental Changes in Aquatic Systems**

#### **3.3.1. Groundwater**

Insufficient data were available to evaluate the mean concentration of nitrates in European groundwaters in 1958, but if it is assumed that the concentration has increased at the same rate as leaching, nitrate content in groundwaters rose from 15 mg l<sup>-1</sup> in 1958 to 45 mg l<sup>-1</sup> in 1984.

#### **3.3.2. River waters**

During the last decades, substantial increases of NO<sup>-</sup><sub>3</sub> concentrations have been recorded in most European rivers: +38% in the Moselle River (Kattan, et. al., 1986) and +78% in the Garonne river (Etchanchu, 1987) during the period 1971-1983; +71% in the Danish rivers (Hagebro, et. al., 1983) between 1967 and 1981. The nitrate concentration in the Rhine River rose from 3.5 mg l<sup>-1</sup> in 1950 to 16 mg l<sup>-1</sup> in 1980 although it was nearly stable before 1950.

On the European scale, the total amount of nitrate exported by the rivers has increased at the same rate as that found for leaching; thus by a factor of 2.8 to 3 between 1950 and 1984. Then, we estimate that mean nitrate concentrations in European rivers increased from 2 to 6 mg l<sup>-1</sup> in 1950 to 12 to 18 mg l<sup>-1</sup> in 1984.

#### **3.3.3. Marine waters**

It was not possible to quantify the ecological consequences of increased inputs of nitrogen in marine ecosystems over the last 30 years, since other contaminants such as heavy metals or pesticides are also responsible for ecological disequilibria. Moreover, historical surveys of marine ecosystems are fragmentary. Nevertheless, some obvious shifts in nitrogen levels and phytoplanktonic communities in the North Sea were stressed during an international conference (Ministerial Declaration, 1987):

- 1) In 23 years, near Helgoland (North Germany), the winter value of total inorganic nitrogen increased 1.7-fold (nitrate increased almost four-fold) and phosphate 1.5-fold, while the dissolved silica level remained constant.
- 2) At the same time, carbon present in silicate-independent flagellates increased six-fold while carbon in silicate-dependent diatoms decreased by one half.

Thus, the increase in phytoplankton biomass has been accompanied by a big shift in species composition from diatoms to flagellates. It was also observed that the trends of phytoplankton increase were exponential while trends in nutrient concentrations were linear. This could be explained by a more efficient utilization of nutrients by flagellates compared to diatoms.

#### 4. NOT IMPOSSIBLE CHANGES IN THE NEXT CENTURY

##### 4.1. Extrapolation of Current Trends up to 2010

The time up to 2010 was chosen for this scenario because the statistical data were taken from 1958, the year the Agricultural Yearbook begins to 1984, and the time span between 1984 and 2010 is equivalent to the time between 1958 and 1984.

Based on the statistical relationships between past and current inputs and outputs in European soils, the nitrogen balance for 2010 was calculated (Figure 24). The calculations assumed linear relationships, which may underestimate the amount of leaching. For example, according to some Swedish studies an increase of chemical fertilizer application above  $100 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  could lead to higher leaching than that estimated from the linear relationship (L. Kauppi, IIASA, personal communication, 1987). The mean rate of chemical fertilizer application calculated for 2010 is  $77 \text{ kg N ha}^{-1}$  of total area, i.e.  $126 \text{ kg N ha}^{-1}$  of agricultural area. Even if leaching is underestimated, we still calculate a drastic increase in losses of nitrogen from the agricultural system to the aquatic system. With a 1.6-fold increase in leaching, the mean concentration of nitrate in the groundwater would reach  $80 \text{ mg NO}_3^- \text{ l}^{-1}$  (with values of  $385 \text{ mg NO}_3^- \text{ l}^{-1}$  in some agricultural areas), well above the E.E.C.'s drinking-water standard. The mean concentration in river water would exceed  $30 \text{ mg NO}_3^- \text{ l}^{-1}$ . Although about 50% of the nitrogen leached from agricultural land is discharged to coastal ecosystems during winter months, in some rivers having long residence times (as with hydro-electric power plants, dams), and with a simultaneous increase of phosphorus levels (Behrendt, 1988) episodes of eutrophication would probably increase. The increasing losses to the environment would lead to nitrogen enrichment of coastal waters (about 60% if we consider the actual contribution of denitrification in freshwaters and estuaries). As we have seen, the problems caused by increasing nitrogen losses from European agriculture are not only high nitrate concentrations in groundwater, but also ecological disequilibria in the aquatic environment as a whole. Therefore it seems necessary to adopt a global approach to the agricultural system in order to take into account the interactions that exist between the different parts of the biosphere.

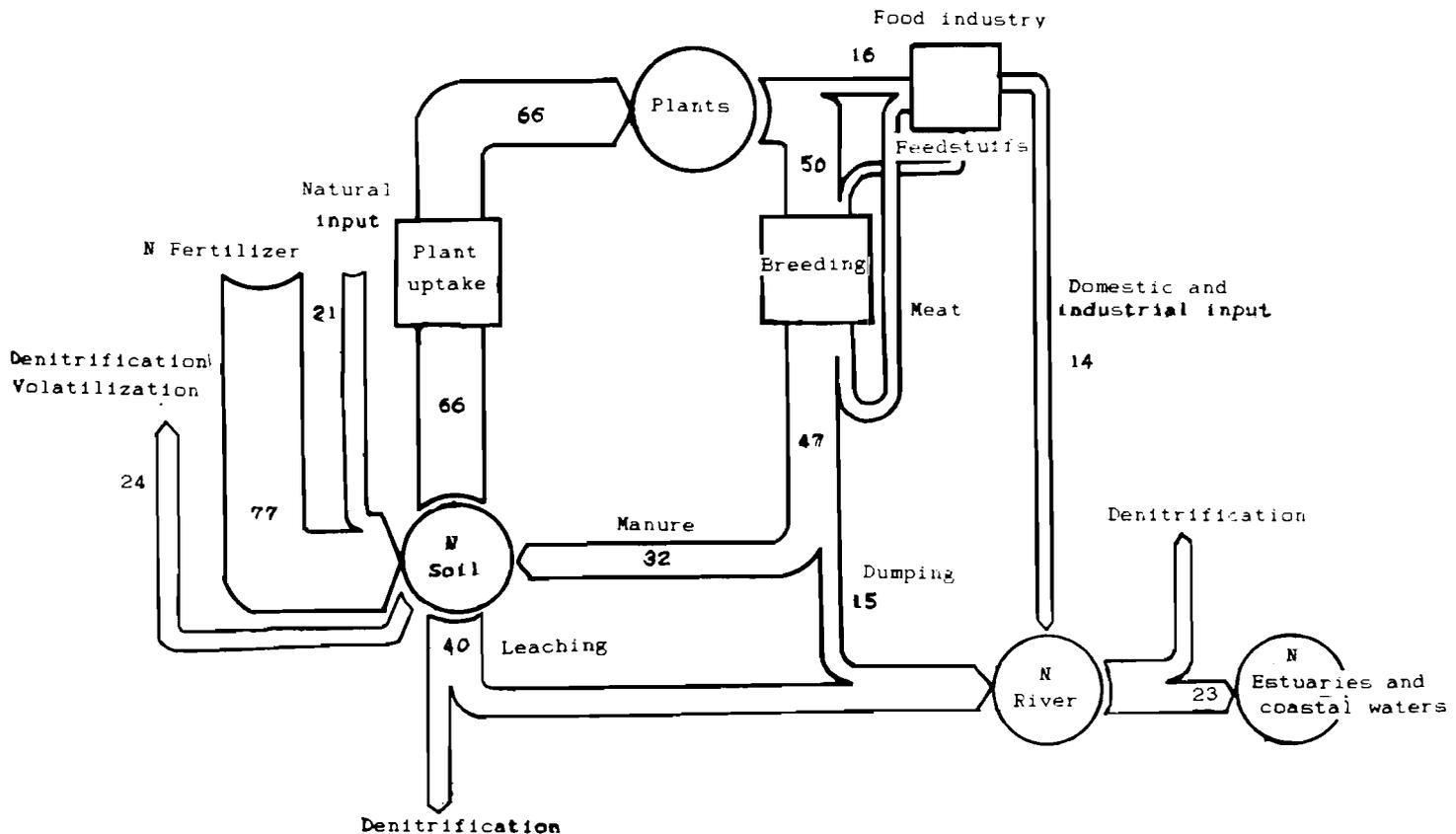


Figure 24 Calculated nitrogen cycle in Europe in 2010 extrapolated from current trends, in  $\text{kg ha}^{-1} \text{ yr}^{-1}$  (of total area).

#### 4.2. Nitrogen Fluxes in Relation to Agricultural Problems

The problems caused by nitrogen losses in the aquatic environment are now well known, and measures are being taken in some European countries against excessive fertilizer application (e.g. high taxes on the purchase of chemical fertilizers). Thus, it would be rather surprising if the actual losses in 2010 were as high as the above estimate. The application of new, less wasteful technologies, as well as economic and structural changes will certainly alter nitrogen cycling in agriculture in the next century. Nevertheless, in order to foster sustainable development, it will be necessary to take a more global view concerning the management of the nitrogen-stock for enhancing agricultural productivity.

As shown in Figure 25, the agricultural system is regulated by activities within the anthropogenic sphere. Energy is expended to make nitrogen fertilizer. The atmosphere is the source of nitrogen. The fertilizer industry transforms molecular nitrogen into chemical fertilizer in the forms of ammonium and nitrate. The fertilizer is added to the soil in large amounts, and some of the nitrogen is returned to society as a component of foodstuffs (vegetables and livestock). Nitrogen is lost from the anthropogenic sphere to aquatic systems during the discharge of domestic and industrial sewage. It is important to note, however, that nitrogen fluxes between the anthropogenic sphere and the agricultural system are small compared to the fluxes within the agricultural system itself.

The agricultural system, and especially the soil, is the place where the nitrogen transformation processes are most important. The soils receive large inputs (chemical fertilizer, manure), and much of these are transported to the aquatic reservoir by leaching. Thus, viewing the system as a whole, the main problems result from leaching of nitrogen, owing to a global, human-driven, nitrogen-flux from the atmosphere to the aquatic environment.

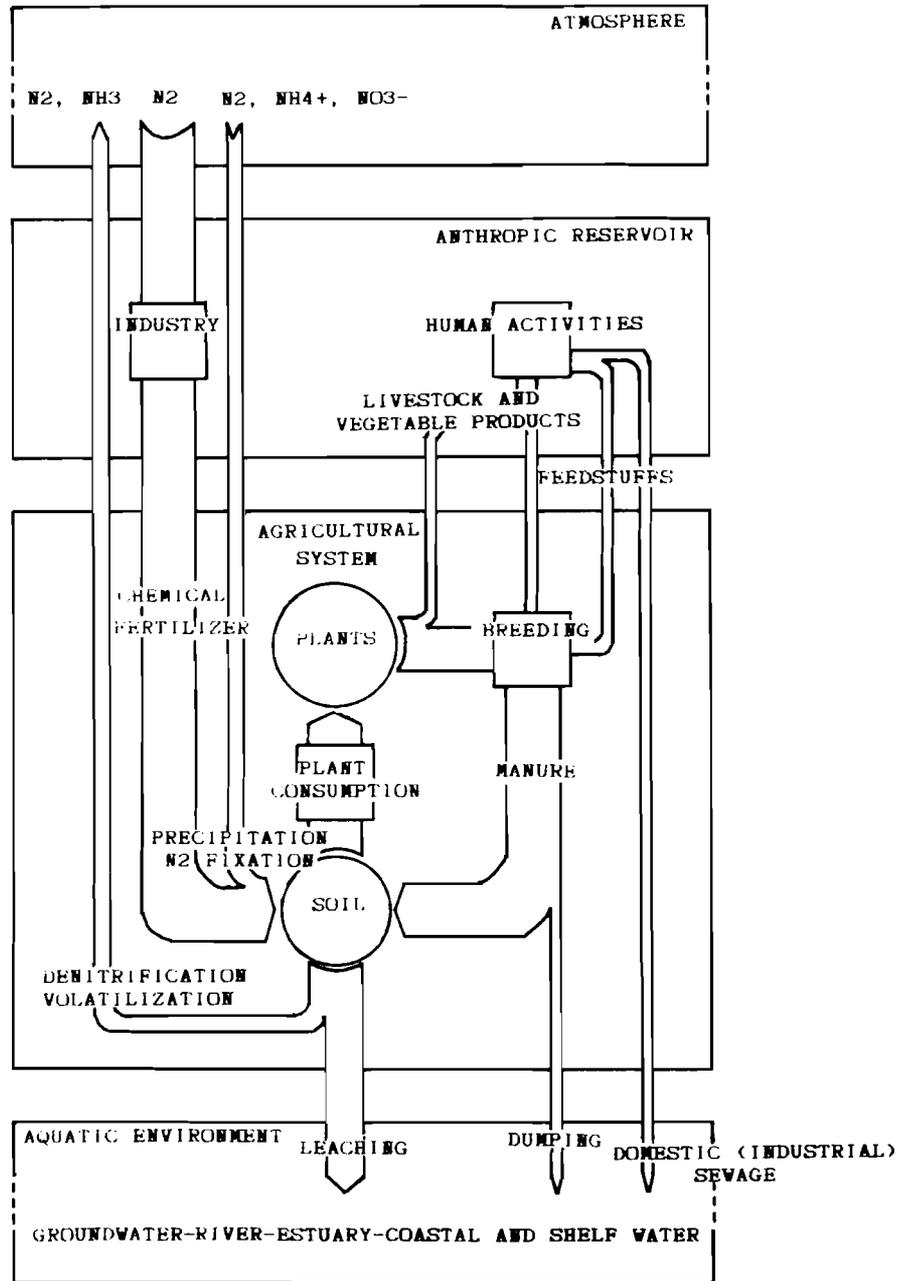


Figure 25 Nitrogen fluxes in the biosphere as influenced by human activities.

### 4.3. Agriculture and "New-Technologies"

The three principal sources of excess nitrogen in aquatic systems are: (1) chemical fertilizers; (2) manure; and (3) domestic sewage. The most interesting new technologies are those which foster more efficient utilization of chemical fertilizers on one hand, and a higher degree of recycling of organic nitrogen (i.e., manure, domestic sewage) on the other hand. Although some short-term solutions have been proposed in order to reduce the high-nitrate concentrations found in aquatic systems (e.g., denitrification, dilution by "clean" water), the problem of eutrophication in rivers and marine waters still remains. Thus, it is mandatory to develop technologies that improve the aquatic environment as a whole.

#### 4.3.1. Soil leaching and nitrogen fixation

Owing to leaching, the residence time of nitrates in soils is short and this form of nitrogen is available for the plants only during a short period. In order to mitigate the leaching problem a first step could be to reduce the quantity of chemical fertilizer applied by half; i.e., from 74 to 37 kg ha<sup>-1</sup> yr<sup>-1</sup> of agricultural area (45 to 22 kg ha<sup>-1</sup> of total area). The direct effect would be a decrease of the plant uptake by 30%. In order to maintain the same production, it would be necessary to increase the percentage of agricultural land in Europe from 61% to 87%. Such an increase, however, is not likely to occur.

Chemical fertilizers are usually spread in large quantities one or two times per year. A good way of limiting losses would be to apply smaller quantities of fertilizer over longer periods of time. Currently this method would increase the costs of production. However, the nitrogen-fertilizer industry is developing granulated forms which release nitrates more slowly (L. Kauppi, IIASA, 1987, personal communication). Thus we may expect an improvement in the efficiency of plant uptake of nitrogen fertilizers in the future.

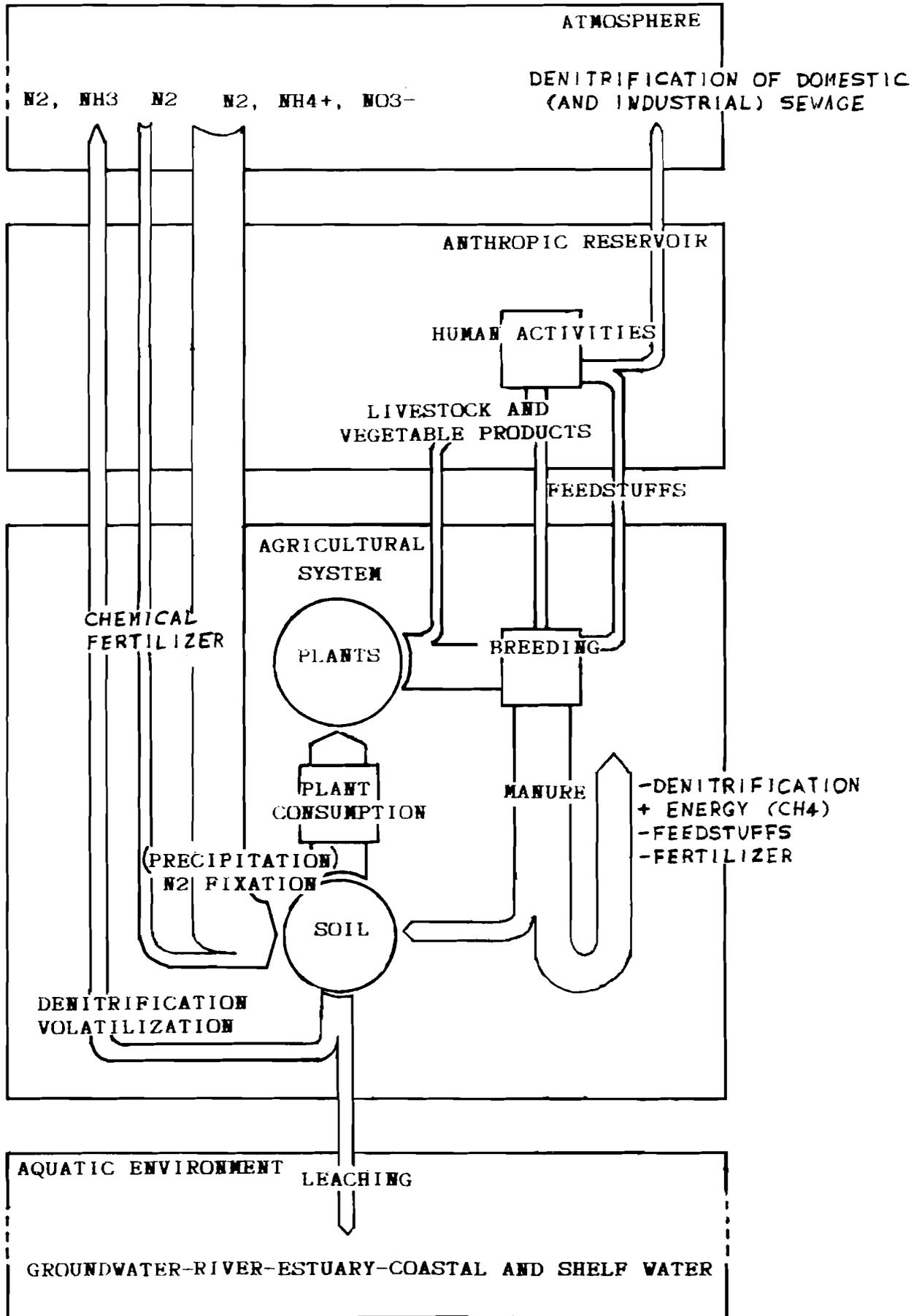
With regard to the biotechnologies, much research is focused on developing nitrogen-fixing bacteria that will live in symbiosis in the roots of cereals, much as they do currently for legumes. However, it is still not known whether such bacteria can actually be developed. If there is a breakthrough in this technology, use of synthetic nitrogen fertilizers would be drastically reduced, with large benefits for the environment and considerable savings in energy. This would be particularly true if the nitrogen uptake were highly efficient with little loss of nitrate to the environment.

Assuming the same levels of agricultural and livestock production are maintained, the accumulation of manure in the agricultural system will not change, even if solutions are found for the problem of leaching of chemical fertilizers. In fact, if nitrogen-fixing cereals are developed as described above, the problem may worsen since manure would no longer be an important source of fertilizer for cereals. Thus, a strategy would have to be devised for utilizing the manure before it leaches into water systems.

#### 4.3.2. Manure and waste treatment

While the solution for limiting losses of nitrogen fertilizer by leaching depends mainly on the development of new technologies, the solution concerning pollution from excess manure relates more to a rigorous policy for treating organic wastes. Efficient methods for transforming manures into good nitrogen fertilizers exist. Broadscale use of manure-derived fertilizer would transform a current waste problem into a valuable resource.

For example, earthworms, using manure as a source of food, produce a rich compost which is already used for fertilization of golf-links, playgrounds and market gardens. This compost generally contains organic nitrogen in part which is slowly mineralized, and therefore not easily leached. The worms can also be recovered and used as a protein source for livestock feed. Similarly, some vegetable species which are a potential source of food for cattle can be grown on the manure. By producing feedstuffs from manure, crops currently allocated for livestock could be reduced and therefore fertilizer inputs as well. Hence, such recycling of manure into compost and feedstuff could allow for a twofold reduction in inputs of chemical fertilizer.



NEW TECHNOLOGIES :  $N_2$  FIXATION - WASTE TREATMENT (DENITRIFICATION)

Figure 26 Possible impact of new technologies on the future nitrogen fluxes in the biosphere.

On the other hand, if nitrogen-fixing cereals are developed, manure will not be necessary for fertilization, and will constitute an excessive stock of nitrogen. It thus will be necessary to denitrify this nitrogen in order to balance the nitrogen fluxes between the different parts of the biosphere (Figure 26).

In this case, the manure can be treated by microbial processes for the production of methane. This method has the advantage of recovering energy while denitrifying the excess nitrogen. Domestic sewage should be similarly treated before being discharged into the aquatic environment.

#### 4.3.3. Conclusion

Many factors affect the nitrogen cycle in European ecosystems. Economic considerations are very important. Currently in the European Community, agriculture is highly subsidized by the member states, even though there is approximately a 20% level of over-production. If subsidies are reduced in the future (which is quite likely), there could be a large decrease in production, and hence in inputs of nitrogen fertilizer to the soil.

The nitrogen cycle can also be influenced by structural changes. An evolution toward extensive agriculture with lower chemical inputs per hectare and more land under cultivation (in order to maintain an overall constant level of production) is unlikely in so far as there is little extra land available for cultivation. In fact, the actual trend toward more intensive agriculture, and the conversion of marginal agricultural lands to forests is envisaged.

Even if nitrogen-fixation by cereals is not developed, fertilizers that release nitrogen more slowly to the environment (resulting in more efficient uptake by plants) will become available, and should be used. Moreover, a more efficient recycling of manure can and should be adopted (Figure 26). The reduction of nitrogen in excess manure by microbial processes should equal the inputs of atmospheric origin (natural nitrogen fixation or chemical fertilization).

## 5. CONCLUSIONS

In European ecosystems, the nitrogen cycle is strongly influenced by agricultural practices. This study has shown relations between agricultural activity and environmental problems. The losses of nitrogen by leaching not only cause high nitrate concentrations in groundwaters, but also ecological disequilibria in coastal waters.

The disruption of the natural nitrogen cycle appears to be proportional to the scale of agricultural activity. The actual situation displays a disequilibrium of nitrogen fluxes from the atmosphere to the aquatic environment, and this trend will have to change in order to avoid ecological and economic problems in the next century.

The solutions depend on: (1) the development of new technologies such as nitrogen fixation by cereals; and (2) the promotion of more efficient recycling of nitrogen within the agricultural system itself.

## REFERENCES

- Alfoldi L., 1983. Movement and interaction of nitrates and pesticides in the vegetation cover - soil groundwater - rock system. *Env. Geol.* 5, 1, 19-25.
- Asman A.H.W and Janssen A.J. 1986., A long range transport model for ammonia and ammonium for Europe and some model experiments. IMOU report R-86-6, pp 79.
- Ballay, Martin, Sebillotte and Tricard. 1985., Rapport francais "les nitrates dans l'eau". SITE 1985.
- Behrendt, H., 1988. Changes in nonpoint nutrient loadings into European freshwaters: trends and consequences since 1950 and not-impossible changes until 2080. IIASA Working Paper: April 1988 WP-88-026.
- Belamie R., 1983. Etude des pollutions diffuses en territoire rural. Elements de methode. Application a l'etude des bassins versants representatifs. Colloque sur l'eutrophisation et la pollution du Lemman, Lyon, 31 aout / 3 sept 1983.
- Billen G., Somville M., de Becker E. and Servais P., 1985a. A nitrogen budget of the Scheldt hydrographical basin. *Neth. J. Sea Res.* 19, 223-230.
- Billen G., De Becker E., Lancelot C., Servais P., Somville M. and Stainier E., 1985b. Etude des processus de transfert, d'immobilisation et de transformation de l'azote dans son cheminement depuis les sols agricoles jusqu'a la mer. Rapport C.E.E., contract ENV-522-B (RS), pp 100.
- Billen G., Toussain F., Peeters P., Sapir M., Steenhout A. and Vanderborcht J.P., 1983. L'Ecosysteme Belgique. Essai d'ecologie industrielle. CRISP, pp 163.
- Brault D., Queguiner B. and Briand X., 1986. Influence quantitative des sels nutritifs azotes sur la croissance d'*Ulva* sp. Final report contract ENV 825F AZOC 2, 99-122.
- Buijsman E., Maas J.F.M. and Asman W.A.H., 1985. Ammonia emission in Europe. IMOU report R-85-2, pp 28. Buttermore R.E., 1977. Eutrophication of an impounded estuarine lagoon. *Mar. Poll.* 8, 13-15.
- C.C.E., 1978. Commission des Communautés Européennes. L'épandage des effluents d'élevage sur les sols agricoles - dans la Communauté Européenne. I. Bases scientifiques pour une limitation des épandages et critères pour des dispositions réglementaires. Série Informations sur l'agriculture, 47 (Luxembourg). Office des publications officielles des Communautés Européennes.
- Champ D.R., Gulens, and Jackson R.E., 1979. Oxidation-reduction sequences in groundwater flow systems. *Canad. J. Earth Sci.* V. 1, 12-23.
- Commission of the European Community, 1982. Groundwater Resources of the European Community. Synthetic Report, pp 75.
- Correll D.L. and Ford D., 1982. Comparison of precipitation and land runoff as sources of estuarine nitrogen. *Est. coast. shelf. Sci.* 15, 45-56.
- Croatto U., 1982. Energy from macroalgae of the Venice lagoon. Proceedings of the International Conference on Biomass. 20-23 September 1982. Berlin. 329-333.
- Cullen J.J. and Horrigan S.G., 1981. Effects of nitrate on the diurnal migration, carbon to nitrogen ratio, and the photosynthetic capacity of the dinoflagellate: *Gymnodinium splendens*. *Mar. Biol.* 62, 81-82.
- Dermine B., 1985. Bilans des charges en nutriments charries au long du cours de la Meuse belge. These de doctorat, Universite Namur, pp 183.
- Duce R.A., 1985. The impact of atmospheric nitrogen, phosphorus and iron species on marine biological productivity. NATO. Advanced study on the role of sea-air exchange in geochemical cycling. Bonbannes (France).

- Durand R., 1978. La pedogenese en pays de craie dans le Nord-Est de la France. These, Univ. L. Pasteur Strasbourg, pp 176.
- Edward P., 1972. Benthic algae in polluted estuaries. *Mar. Poll. Bull.* 3(4), 55-60.
- Egboka B.C.E., 1984. Nitrate contamination of shallow groundwaters in Ontario, Canada. *The Science of the Total Environment*, 35, 53-70.
- Etchanchu D., 1987. Geochimie du bassin de la Garonne. Transferts de matieres et particulaires par le fleuve vers l'ocean Atlantique. These doctorat, Toulouse III, en preparation.
- Etchanchu D. and Probst J.L., 1986. Dynamique et origine des nitrates sur un bassin agricole du sud ouest de la France: le Girou. *Congress Ass. Fr. Limn., Thonon les Bains*, 28-30 mai 1986, pp 15.
- Eurostat, 1971-1985. *Fertilizer Yearbooks*.
- Faurie G., 1977. Etude in vitro du role de la nitrification sur la lixiviation du calcium dans les sols calcaires. *Science du sol*, 4, 204-218.
- Fitzgerald W.J., 1978. Environmental parameters influencing the growth of *Enteromorpha clathrata* in the intertidal zone on Guam. *Bot. Mar.* 21, 207-220.
- Fonda Umami S., 1985. Hydrology and "Red Tides" in the gulf of Trieste (North Adriatic Sea). *Oebalia*. 11, 141-147.
- Frostick L.E. and McCave I.N., 1979. Seasonal shifts of sediments within an estuary mediated by algal growth. *Estuar. and coast. sci.* 9, 569-576.
- Garcon V., Stolzenbach K.D. and Anderson D. M., 1986. Tidal flushing of an estuarine embayment subject to recurrent dinoflagellate blooms. *Estuaries* 9(3), 179-187.
- Grennfelt P. and Hultberg H., 1986. Effects of nitrogen deposition on the acidification of terrestrial and aquatic ecosystems. *Water, Air, Soil Poll.*, 30, 945-963.
- Greve W. and Parsons T.R., 1977. Photosynthesis and fish production; hypothetical effects of climatic changes and pollution. *Helgolander wiss. Meeresunters.* 30. 666-672.
- Gustafson A., 1983. Leaching of nitrate from arable land into groundwater in Sweden. *Env. Geol.*, vol.5, 2, 65-71.
- Guzman L. and Campodonico I., 1978. Mareas joras en Chile. *Interciencia*. 3(3), 144-151.
- Hafsaoui M., Queguiner B. and Treguer P., 1985. Production primaire et facteurs limitant la croissance du phytoplancton en rade de Brest (1981-1983). *Oceanis*, 11(3), 181-195.
- Hagebro C., Bang S. and Somer E., 1983. Nitrate load/discharge relationships and nitrate loads trends in Danish rivers. *Proc. of the Hamburg symp., I.A.H.S publ.* 141, 377-386.
- Hanson S. and Gilfillan E.S., 1975. Effects of polluted and non polluted sediments on the growth of *Gonyaulax tamarensis*. *Environ. Let.* 9(1), 33-41.
- Harlin M.M. and Thorne-Miller B., 1981. Nutrient enrichment of seagrass beds in a Rhode Island coastal lagoon. *Mar. Biol.* 65, 221-229.
- Kattan Z., Salleron J.L. and Probst J.L., 1986. Bilans et dynamiques de transfert de l'azote et du phosphore sur le bassin de la Moselle (Nord-Est de la France). *Sciences de l'eau*, 5, 435- 459.
- Kauppi L., 1984. Contribution of agricultural loading to the deterioration of surface waters in Finland. *Publ. of the Water Research Institute, National Board of Waters, Finland*, 57, 1984.

- Legendre L. and Demers S., 1985. Auxiliary energy, ergoclines and aquatic biological production. *Naturalist can.* 112, 5-14.
- Lowthion D. Soulsby P.G. and Houston M.C.M., 1985. Investigations of an eutrophic tidal basin: part I. Factors affecting the distribution and biomass of macroalgae. *Mar. Environ. Res.* 15, 263-284.
- Margalef R., 1984. Le plancton dans la Mediterranee. *La Recherche.* 15, 1082- 1094.
- Martin-Jezequel V., 1981. Succession des populations phytoplanktoniques en relation avec les conditions nutritionnelles dans les eaux littorales de la Manche. Third cycle thesis, U.B.O., Brest. pp 145.
- Ministerial Declaration, 1987. Second International Conference on the Protection of the North Sea, 24-25 November, 1987, London. Ministers responsible for the protection of the North Sea of the Governments of Belgium, Denmark, France, Federal Republic of Germany, The Netherlands, Norway, Sweden, United Kingdom, and the Member of the Commission of the European Communities responsible for environmental protection.
- Morton B. and Twentyman P.R., 1974. The occurrence and toxicity of a red tide caused by *Noctiluca scintillans* (Macartney) Ehrenb., in the coastal waters of Hong Kong. *Env. res.* 4, 544-557.
- Montgomery H.A.C., Soulby P.G., Hart I.C. and Wright S.L., 1985. Investigation of a eutrophic tidal basin: part 2- Nutrients and environmental aspects. *Mar. Environ. Res.* 15, 285-302.
- Nicholls D.J., Tubbs C.R. and Haynes F.W., 1981. The effects of green algal mats on intertidal macrobenthic communities and their predators. *Kiel. Meeres.* 5, 511-520.
- Nodop K., 1986. Nitrate and sulfate wet deposition in Europe. Proceedings of the Fourth European Symposium on Physico-Chemical Behaviour of Atmospheric Pollutants. Stresa (Italy), 22-25 September.
- Paerl H.W., 1985. Enhancement of marine primary productivity by nitrogen-enriched acid rain. *Nature.* 315, 747-749. Parker M.M., 1980. Red tides. *Mar. Poll. Bull.* 6, 175.
- Partensky F. and Sourina A., 1986. Le dinoflagelle *Gyrodinium* cf. *aureolum* dans la plancton de l'Atlantique Nord: Identification, ecologie, toxicity. *Cryptogamie, Algologie.* 7(4), 251-275.
- Philipps I., 1981. Qualite des eaux de l'estuaire de la gironde. Repartition et comportement des sels minereaux dissous: Azote, phosphore et silice. Third cycle thesis, U.B.1, Bordeaux, pp 179.
- Probst J.L., 1985. Nitrogen and phosphorus exportation in the Garonne basin (France). *J. of Hydrol.*, 76, 281-305.
- Probst J.L., 1983. Hydrologie du bassin de la Garonne. Modele de melange. Bilan de l'erosion. Exportation des phosphates et des nitrates. These doctorat, Universite Toulouse III, pp 148.
- Probst J.L. and Bazerbachi. A. 1986. Transports en solution et en suspension par la Garonne superieure. *Sci. Geol. Bull.*, 39(1), 79-98.
- Queguiner B., 1986. mise en evidence des facteurs limitant la production primaire dans le Mor Braz (Bretagne meridionale). Final report Probras programm, U.B.O., Brest, pp 88.
- Reid P.C., 1980. Toxic dinoflagellates and tidal power generation in the bay of Fundy, Canada. *Mar. Pol. Bul.* 11, 47-51.
- Reise K., 1983. Sewage, green mats anchored by lugworms and the effects on *Turbellaria* and small polychaeta. *Helgo. Meeres.* 36, 151-162.

- Royal Society, 1983. The nitrogen cycle of the United Kingdom. Study Group Report, pp 264.
- Schrey S.E., Carpenter E.J. and Anderson D.M., 1984. The abundance and distribution of the toxic dinoflagellate, *Gonyaulax tamarensis*, in Long Island estuaries. *Estuaries*. 7(4B), 472-477.
- Schroder H., 1985. Nitrogen losses from Danish agriculture. Trends and consequences. *Agr. Ecosys. Env.* 14, 279-289.
- Souchu P., 1986a. Contribution a l'etude du cycle de l'azote en ecosysteme macrotidal. Third cycle thesis, U.B.O. Brest. pp 124.
- Souchu P., 1986b. Impact des precipitations sur l'equilibre des systemes littoraux de Bretagne. E.P.R. report, U.B.O. Brest. pp 26.
- Souchu P. and Treguer P., 1986. Influence of dissolved inorganic nitrogen fluxes on western Europe coastal ecosystems. Proceedings of the Fourth European Symposium on Physico-Chemical Behaviour of Atmospheric Pollutants. Stresa (Italy), 22-25 September.
- Soulby P.G., Lowthion D. and Houston M., 1982. Effects of macroalgal mats on the ecology of intertidal mudflats. *Mar. Poll. Bull.* 13, 162-166.
- Treguer P., 1984. Evolution des composes de l'azote organique et inorganique dans un estuaire soumis a des pollutions d'origine agricole. Contrat C.N.E.X.O. 83/7019, pp 105.
- Tester D.J., Chem C., and Carey M.A., 1985. The prediction of nitrate pollution in chalk groundwater-derived potable supplies and the renovation of an affected source. *Wat. Pollut. Control* 1985, 366-379.
- Warfe J.R., 1977. An ecological survey of the benthic invertebrate macrofauna of the lower medway estuary, Kent. *J. Anim. Ecol.* 46, 93-113.
- Wilkinson L., 1963. Nitrogen transformation in a polluted estuary. *Int. J. Air. Wat. Poll.*, 7, 737-752.
- Wollast R., 1983. Interactions in Estuaries and Coastal Waters. In, *The Major Biogeochemical Cycles and Their Interactions*, B. Bolin and R.B. Cook (eds.). SCOPE series, New York, John Wiley.
- Wollast R., 1982. Behaviour of organic carbon, nitrogen and phosphorus in the Scheldt estuary. *Thalassia Jugosl.* 18, 11-34.
- Wollast R. and Duinker J.C., 1982. General methodology and sampling strategy for studies on the behaviour of chemicals in estuaries. *Thalassia Jugosl.* 18, 471-491.
- Wollast R. and Peters J.J., 1980. Transfer of materials in estuarine zones. Proceedings of the Symposium on Transport Processes in Estuarine and Near-Shore Zones. International Council for the Exploration of the Sea 68th Statutory Meeting. Copenhagen, Denmark, October.
- Wollast R. and Peters, J.J., 1978. Biogeochemical properties of an estuarine system: the river Scheldt. In *Biochemistry of Estuarine Sediments*, E.D. Goldberg (ed.). UNESCO, Paris, 279-293.
- Yusop M.K., Van Cleemput O. and Baert L., 1984. Nitrogen fertilization and nitrate pollution of groundwater in sandy soils. *Env. Pollut.(series B)*, 7, 43-48.
- Zwolsman G., 1986. Nutrient biogeochemistry in estuaries, with an emphasis on the Scheldt estuary. Student report. Fac. Geol., Utrecht, pp 85.