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J. Vrba/E. Romijn

Impact of Agricultural Activities on Ground Water

**Volume 5
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International Contributions to Hydrogeology

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G. Castany, E. Groba, E. Romijn

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PREFACE

Groundwater is generally a renewable natural resource. The processes of groundwater formation are perceptible in a human time-scale. Groundwater resources are subject to a continuous process of recharge and discharge, both natural and artificial. Short-term shallow circulation of groundwater is the main cause of aquifer vulnerability with respect to contamination.

Groundwater protection should be considered an integral part of national or regional water planning and management. This means that the task of groundwater protection should be undertaken simultaneously with investigation and development of groundwater resources. In cases where an aquifer will be, or is already being used, for water supply, a detailed study of groundwater protection requirements is particularly important.

In the International Association of Hydrogeologists, IAH, the impact of human activity on groundwater systems and the theoretical and practical problems of groundwater protection have been subjects of attention for many years. Since 1972, several IAH Congresses and International Symposia have dealt with topics related to groundwater pollution protection problems.

In 1979, the Commission for Groundwater Protection of IAH was established. To date its activity has concentrated upon study of the impact of petroleum on groundwater quality, on the impact of agricultural activities on groundwater, on groundwater protection zones and on integrated land-use planning and groundwater protection management in rural areas.

In project on "Impact of Agricultural Activities on Ground Water" was part of the IAH contribution to the 2nd phase of the International

Hydrological Programme. The scope of the project included international symposium, workshop and a monograph.

The International Symposium on "Impact of Agricultural Activities on Groundwater Quality and Quantity", held in Prague, Czechoslovakia, in September 1982, was sponsored by the IAH and the Czechoslovak Government in cooperation with UNESCO, UNEP and other international organizations.

In the course of the symposium, nearly 100 papers were presented and discussed concerning the following themes: pesticides and disease-producing bacteria in groundwater; movement and interaction of nitrates and pesticides in the vegetation cover-soil-groundwater-rock system; mathematical modelling of the agricultural impact on groundwater quality and quantity; the impact of drainage and irrigation on groundwater. Round table discussion dealt with the legislative needs to resolve conflicts between agricultural activities and groundwater interests. Some papers presented at the symposium were selected for the second part of the Monograph as case histories.

All members of the Commission for Groundwater Protection took an active part in the preparation of this Monograph. A great number of stimulating ideas and recommendations concerning its content arose from discussion at sessions of the Commission in the years 1980 - 1983. Colleagues from the United Kingdom, especially Mr. J.B.W. Day undertook linguistic revision of text. Mr. J.C. Miller from the USA reviewed the case histories.

Last but not least, I would like to express - on behalf of the Commission - our thanks to Mr. J.S. Gladwell, senior programme officer of UNESCO - Water Science Division, who cooperated actively in the realization of the whole IHP/UNESCO project A.3.7 "Impact of Agricultural Activities on Ground Water".

Prague, November 1985

Dr. J. Vrba.

Permanent members of the I.A.H. Commission for Groundwater Protection

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INTRODUCTION

About 10,000 years ago, hunting man became farming man. The first seeds were sown, animals were domesticated and agriculture, one of the greatest developments in man's history, began. Due to insufficient mechanization and fertilization the yield of cereals and other crops remained at a low level for a long time. At the beginning of the 19th century, wheat yields in Europe had only reached one tonne per hectare; 75% of population being engaged in agriculture at this time. Until the beginning of the 1940's, organic fertilizers were mostly used and the additions of nitrogen to the soil barely exceeded 10 kg per ha per year. However, by the end of the same decade, applications of nitrogen had grown threefold. Another increase in fertilizer applications occurred in the years of the so-called "green revolution" (1960-1970) when consumption of inorganic fertilizers doubled, and the quantity of applied nitrogen in most European countries reached over 60 kg per ha per year. In developed countries, the proportion of the population working in the agricultural sector decreased concurrently to about 10%.

The effort of nations to reach self-sufficiency in the production of cereals (a strategic concern in the economic and political sense) required a continuous increase of agricultural production. The economic interests in agriculture, one of the most important sectors in most countries, became of the foremost significance. The ecological consequences of agricultural activities were pushed into the background. The reason for this is the fact that economic return in the form of high crop yields is immediate, while negative impact on the ecosystem (and especially on the groundwater system) is not usually felt until after the lapse of a long period of time. Unfortunately our knowledge of the interaction between the eco and agro systems is not yet sufficient to allow accurate forecasting of the

long-term impact of agricultural activities on groundwater systems. In the course of several millennia the original ecosystem and geosystem have been changed by man's agricultural activities. The gradual transformation of the ecosystem caused by ploughing, sowing, fertilizing, irrigation and drainage affected interactions between vegetation, soil, water and rock. Deep ploughing, the use of heavy machines, inorganic fertilizers, pesticides and irrigation are improving agricultural productivity, however a negative impact on the quality of water and the state of the soil is also apparent. Groundwater pollution, desertification, salinization and water logging of soils are examples of negative impact.

The widespread incorrect use of fertilizers has produced "nitrogen contamination" of the hydrogeological system and also of plants, notably vegetable crops. The negative effects of excessive nitrate intake on the human health have been recognized.

The increase of nitrate concentrations in groundwater has been mainly observed in regions of arable land with sandy soils, a shallow groundwater table and high permeability aquifers. The nitrate concentrations of groundwater in such cases frequently exceeds 50 mg/l, with yearly increases of 0.5 to 1.5 mg/l.

It must be emphasized that the current fertilizer applications lead to a high risk of nitrate concentrations in groundwater exceeding the current WHO recommendations of 50 mg/l. From this point of view, the amount of fertilizers used, selection of suitable kinds, determination of doses, especially chemical nitrification inhibitors are important to minimize fertilizer losses from the plant and soil system to groundwater.

Crop yields are reduced by plant diseases, insects and weeds. According to UN data, yields are lowered by 22% through such losses, other sources estimate up to 35%. The possible negative impact of pesticides on the environment, including the hydrogeological system, has been for some time recognized. Properties such as persistence, mobility, biodegradation, bioaccumulation and toxicity need intensive

investigation. The organochlorine group are exceptionally persistent in the environment, and the mobile organophosphorus and carbamates compounds are also a potential threat to groundwater systems.

So far only a few cases have been described of groundwater pollution by pesticides. However, effects of pesticides on the quality of groundwater must be paid constant attention, and ways of reducing the environmental effect of pesticide application developed.

Irrigation and drainage have an important place in present day agriculture, Long-term soil irrigation can result, under certain climatic conditions, salinization in soil and groundwater. Salinization as a consequence of irrigation was known in the ancient civilizations between the Euphrates and Tigris rivers and along the Nile valley. Today large areas, the San Joaquín Valley of the USA and the Karakum region of the USSR, amongst others, are threatened by soil salinization. Some 250 million hectares of soil are currently irrigated in the world, this represents about 17% of world farm land. According to different sources, almost a half of this area is affected by salinity and water logging due to irrigation. Irrigation effectiveness is often very low and, on permeable land, much recharges the aquifer. This often has a negative effect on groundwater quality. This is a very serious economic and ecological problem, because irrigated agriculture uses about 80% of the world's developed water resources.

Intensive livestock farming produces enormous quantities of liquid and solid manure and slurry which highly exceeds the needs of the farm. In such cases an overfertilizing exists which should be called "waste disposal". Leakage from manure stockpiles are often sources of bio-organic pollution of the groundwater system.

It is evident that the relationship between agricultural land use and groundwater protection is complex and conflict of interests between agriculture and water use is frequent. Management and optimization of relations between those sectors are desirable and require a specific

approach in each agricultural region. The following motto was emphasized in course of the Prague symposium in 1982 on "Impact of Agricultural Activities":

"The destiny of bread and water on this earth lies in the man's hands. The future must be secured by harmonizing the natural ecosystem, as hunger and thirst are the two greatest disasters which can affect man's life".

1. THE ATMOSPHERE-SOIL-PLANT SYSTEM AND THE WATER CYCLE

E. ROMIJN

1.1. INTRODUCTION

In order to study the affects of agriculture on groundwater quantity and quality the agricultural system has to be divided in different subsystems. These are often the subject of very specialized branches of science. Therefore only some salient facts can be described in this monograph, stressing the hydrogeological point of view.

Some of the subsystems to be distinguished are:

a) "Abiotic" subsystems

- atmosphere, climate and weather,
- the hydrological cycle (including irrigation and drainage),
- the soil and sub-soil,
- geochemical cycles (including fertilizing),
- energy flow.

b) "Biotic" subsystems

- crops and their biochemistry,
- micro organisms,
- animal life directly connected with crops: insects, cattle etc.

c) "Human" subsystems

- type of farm,
- technology used,
- socio-economic circumstances.

As one can see, the abiotic, biotic and human subsystems are interconnected, they influence each other. Consequently, one cannot speak straightforwardly of the impact of agriculture on groundwater quan-

tity and quality. One can only analyze processes and illustrate situations. In the following attention will be given to the abiotic and biotic subsystems only.

1.2. THE ABIOTIC SUBSYSTEM

1.2.1. Evaporation and evapotranspiration (*)

The radiation balance

The main source of energy for the processes in the atmosphere and on the surface of the earth is the sun. Therefore, our short review should start with some remarks on solar radiation and the radiation balance.

The solar energy per unit area, perpendicular to the direction earth-sun, incident on the earth, is called the solar constant S_o , $S_o = 1.39 \text{ kW.m}^{-2}$ (about 2 cal per cm^2 per minute). On the average the earth receives per horizontal m^2 $S_o/4 = 0.35 \text{ kW.m}^{-2}$ (about 0.5 cal per cm^2 per minute).

Actually the distribution is not uniform, the annual value at the equator is about 2.4 times that near the poles. Of the solar radiation 99% falls between 0.15 and $4.0 \mu\text{m}$ wavelength (that is short-wave), 45% is in the visible wavelength range (0.4 to $0.7 \mu\text{m}$). Part of the solar radiation is absorbed and another part is reflected and scattered back by clouds, dust and air molecules (including water vapour); the main part of the scattered radiation reaches the earth as diffuse radiation S_d . Absorption is highest at the wavelength below $0.3 \mu\text{m}$ (due to ozone and molecular oxygen) and above $0.7 \mu\text{m}$ (due to water vapour and carbon dioxide). S_b is the direct beam radiation. From the global radiation ($S_b + S_d$) that reaches the earth's surface the fraction r (albedo) is reflected.

(*) See list of symbols at the end of this chapter.

On the average S_b is about 31% and S_d about 22% of the radiation incident on the top of the atmosphere. The albedo is about 6% for water surfaces, 10 to 25% for vegetation and up to 90% for snow and clouds.

The surface of the earth, heated by the sun, in its turn radiates in the infrared ("longwave") range mainly between 4.0 and 50 μm wavelength. Clouds absorb the longwave radiation, the same holds for water vapour (5.3 to 7.7 μm and $\lambda > 20 \mu\text{m}$), ozone (9.4 to 9.8 μm) and carbon dioxide (13.1 to 16.9 μm). Only about 9% of the outgoing longwave radiation L_u escapes directly to space, mainly through the "atmospheric window" (8.5 to 11.0 μm). The atmosphere also radiates energy (because of absorption of shortwave and longwave radiation), and more than half of it reaches the earth as "counter radiation" L_d . This is called the greenhouse effect. The other part is lost to space.

The effective outgoing radiation of the earth's surface is $L_n = L_u - L_d$ is about 69 W.m^{-2} .

Table 1.1. Radiation balance of the earth, W.m^{-2} (Sellers, 1974).

A. Solar radiation			
1. Incident on top of atmosphere	350	2. Reflected by:	
		- clouds	84
		- molecules, dust, vapour	20
		- earth's surface $r(S_b + S_d)$	<u>21</u>
		Total reflected	125
		3. Absorbed by:	
		- clouds	9
		- molecules, dust, vapour	51
		- earth's surface	
		$(1-r)(S_b+S_d) = S_n$	<u>165</u>
		Total absorbed	<u>225</u>
Total	350	Total	350

B. Infrared radiation			
1. Infrared rad. from		2. Lost to space	225
earth (L_u)	343	Absorbed by atmosphere	316
Infrared rad. from		Counter radiation (L_d)	274
atmosphere	<u>472</u>		—
Total emitted	815	Total	815

To complete the balance, the shortwave radiation received (absorbed) in the earth-atmosphere system is on the average 225 W.m^{-2} and the longwave radiation lost from the system is 69 W.m^{-2} (L_n) plus the net infrared radiation emitted by the atmosphere ($472 - 316 = 156 \text{ W.m}^{-2}$), together also 225 W.m^{-2} . At the other side, the radiation incident at the top of the atmosphere (350 W.m^{-2}) is equal to the reflected solar radiation (125 W.m^{-2}) plus the longwave radiation lost to space (225 W.m^{-2}).

Evaporation

We must return to the radiation balance which controls the evaporation. The available energy of the net radiation flux $R_n = S_n - L_n = (1 - r) (S_b + S_d) - L_u + L_d$ (on the average $165 - 69 = 96 \text{ W.m}^{-2}$) is divided over the heat fluxes for evaporation (LE_m), of sensible heat (H), into the soil (G) and for snowmelt (M). Those used for photosynthesis are relatively small. With ΔF equal to advection or horizontal energy transport:

$$R_n = (1 - r) (S_b + S_d) - L_n = LE_m + H + G + M + \Delta F$$

mostly simplified to:

$$R_n = LE_m + H, \quad L \text{ is latent heat of vaporization.}$$

$$\beta = H/LE_m \text{ is called the Bowen ratio.}$$

According to Sellers (1974) the Bowen ratio increases from 0.05 near the equator to 0.5 at 70° N . Above 70° latitude R_n becomes as yearly

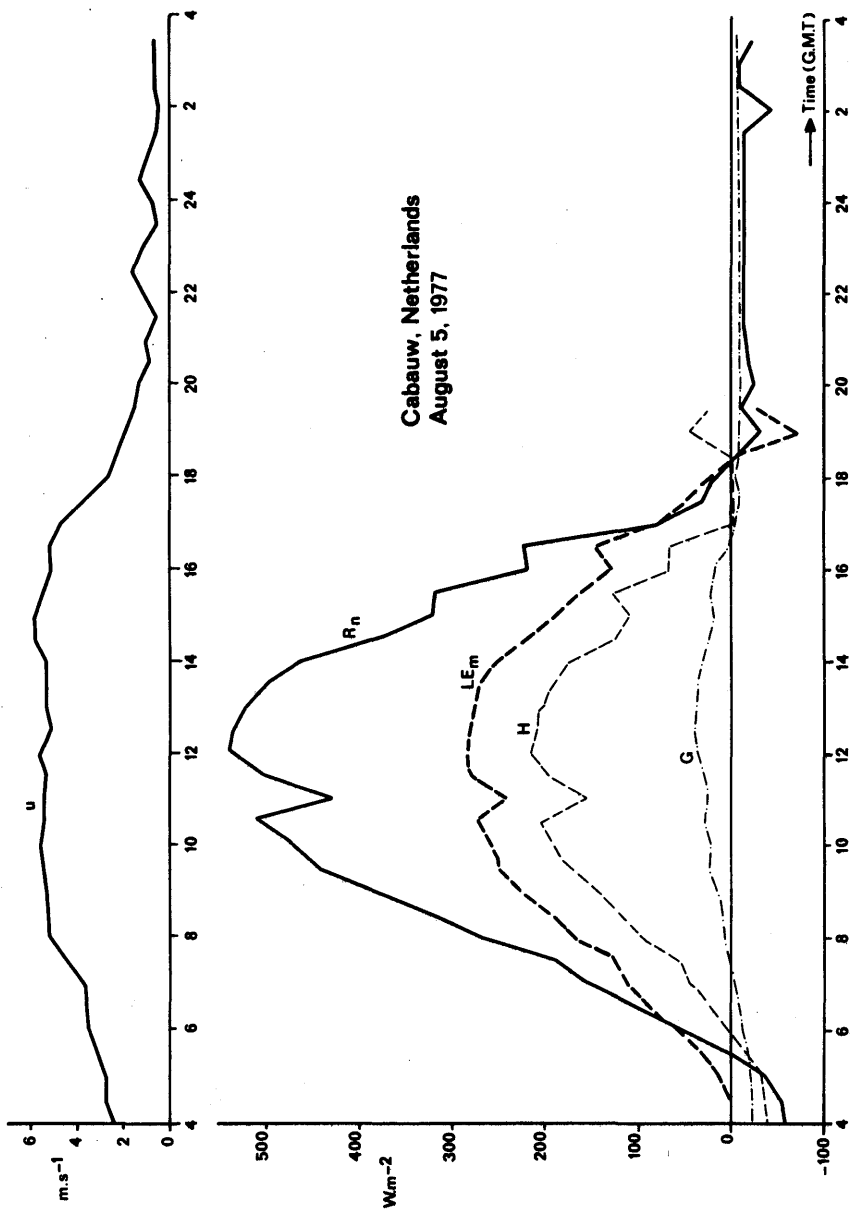


Fig. 1.1.1. Windvelocity u at 2 m height and energy flows on a bright summerday above grassland. KNMI experimental station Cabauw, Netherlands (from De Bruin & Kosiek, 1979).

average negative. In middle latitudes β is about 0.7 for vegetations and 0.1 for water.

The Bowen ratio, expressed in temperature (T) and vapour pressure (e) becomes:

$$\beta = \gamma (T(z_2) - T(z_1)) / (e(z_2) - e(z_1))$$

$$\gamma = p \cdot c_p / 0.62 L = 0.66 \text{ mbar} \cdot \text{K}^{-1} \text{ at sealevel, } \gamma \text{ is called psychrometric constant.}$$

In order to calculate evaporation with help of the Bowen ratio method, T, e, R_n and G have to be measured in the field.

As an example, the average evaporation goes from zero near the poles to 1.5 m per year near the equator. Figure 1.1 gives an example of the energy partition measured by De Bruin & Kosiek (1979) in the Netherlands.

In our treatise we are interested in both the evaporation from open water and the evapotranspiration from vegetation canopies. Penman developed a formula for the calculation of the evaporation from open water in 1948. This formula is based on both the radiation balance and the Bowen ratio. It can be extended to evapotranspiration by introducing a diffusion resistance r_E ($\text{m}^{-1} \cdot \text{s}$) for vapour transport in the air, and a diffusion resistance r_c ($\text{m}^{-1} \cdot \text{s}$) for vapour transport through the vegetation canopy, such that

$$E_m = \{ \rho c_p / \gamma L \} \cdot \{ (e_{so} - e(z)) / (r_E + r_c) \} \quad , e_{so} \text{ is the}$$

saturation vapour pressure for $z=0$ (water surface)

From the Bowen ratio formula it follows that

$$\beta = H / LE_m = \gamma \{ T_o - T(z) \} / \{ (e_{so} - e(z)) / (1 + r_c/r_E) \}$$

and from the radiation balance

$$LE_m = \{s(R_n - G) + \gamma LE_a\} / \{s + \gamma (1 + r_c (\gamma / \rho_m c_p) f(u))\}$$

$W.m^{-2}$

$$f(u) \equiv \rho_m c_p / \gamma r_E, \quad s = (\partial e_s / \partial T) |_T$$

$E_a \equiv (f(u) / L) \{e_s(T(z)) - e(z)\}$ is the drying power of air

graphs for s and γ are given in figure 1.2.

For open water $r_c = 0$ and according to Penman

$f(u) = 7.4 (1 + 0.54 u_2) W.m^{-2}.mbar^{-1}$ with u_2 is equal to the wind-speed measured at 2 m height above the open water. The Lake Hefner studies urged Penman later on to put $f(u) = 7.4 (0.5 + 0.54 u_2)$.

According tot Thom and Oliver (1977) the first Penman wind function results in:

$$r_E = 250 / (1 + 0.54 u_2) m^{-1}.s$$

For rural areas Thom and Oliver took

$$r_E = 100 / (1 + 0.54 u_2) \text{ and } r_c/r_E = 1.4 \text{ which results for}$$

the canopy in:

$$LE_m = \{s(R_n - G) + 2.5 \gamma LE_a\} / (s + 2.4 \gamma) W.m^{-2}$$

The evapotranspiration from a short green crop, without any water shortage, is called the potential evapotranspiration E_p . The Penman "open water" evaporation is called E_o . It turns out that in Western Europe during the growing season (March to September), $E_p = 0.8 E_o$ when calculated with daily (24 h) means for u , T and e . Thom and Oliver estimated for Southern England that $r_c = 65 s.m^{-1}$. Under dryer

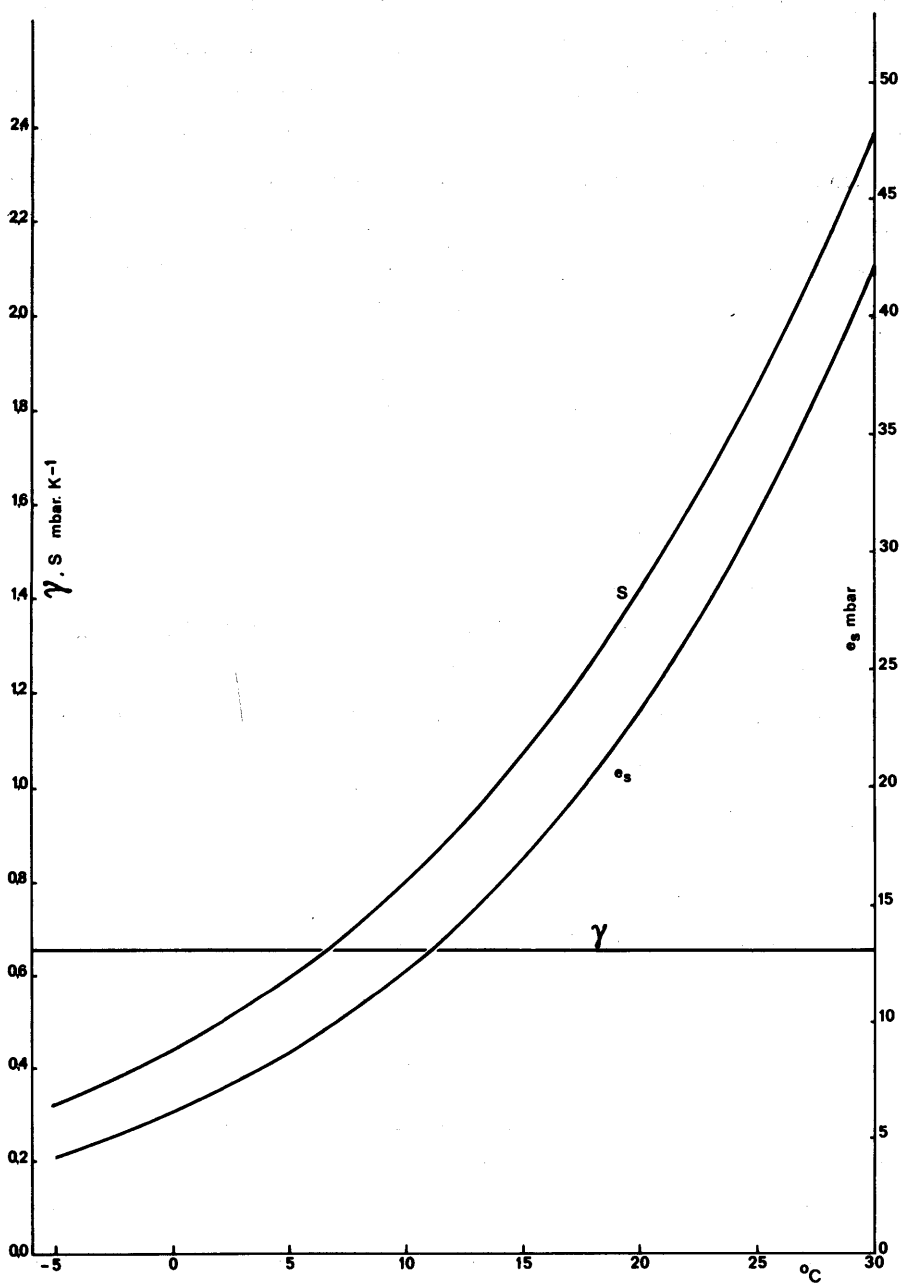


Fig. 1.2. Values of saturation vapour pressure e_s , slope of saturation pressure curve s and the psychrometric constant γ .

conditions, both with respect to soil water (dry soil) or meteorological conditions (high E_o although soil water is not restrictive), r_c becomes greater because the stomata are closing and the actual evapotranspiration $E_A < 0.8 E_o$. Under arid conditions the Penman formula tends to overestimate the evapotranspiration. In this case the Priestley-Taylor (1972) formula could be applied both for open water evaporation and potential evapotranspiration, which formula reads:

$$LE_m = 1.26 \{ s / (s + \gamma) \} (R_n - G) W.m^{-2}$$

1.2.2. The climate and the water balance

As an introduction to the hydrological cycle a rough balance of evaporation E_A and precipitation P in terms of water depth per year are presented in the next table. The data according to Budyko are taken from Sellers (1974).

$U = P - E_A$ is called runoff.

Table 1.2. Global water balance, mm per year.

	E_A	P	U	U/P
all oceans	1250	1120	-130	
all continents	410	720	310	0.43

More specifically, the equatorial zones and the areas poleward of the 40th parallel have overall positive runoff values, whereas the subtropical belt has negative ones.

The climatic zones can be characterized with a number of water balance parameters, e.g. with the runoff ratio U/P , the radiational index of dryness (Budyko) E_o/P and the evaporation ratio E_A/P , $U/P = 1 - E_A/P$.

Table 1.3. Climatic water balance indices according to Budyko (Sellers 1974).

	U/P	E_A/P	E_o/P	E_o/E_A
tundra	> 0.70	< 0.30	< 0.33	< 1.10
forest	$0.30 - 0.70$	$0.30 - 0.70$	$0.33 - 1.00$	$1.10 - 1.43$
steppe	$0.10 - 0.30$	$0.70 - 0.90$	$1.00 - 2.00$	$1.43 - 2.22$
semi-desert	$0.03 - 0.10$	$0.90 - 0.97$	$2.00 - 3.00$	$2.22 - 3.09$
desert	< 0.03	> 0.97	> 3.00	> 3.09

For agriculture, the soil moisture regime during the growing season is most important. $\Sigma (E_p - E_A)$ due to soil moisture depletion is called soil moisture deficiency. A soil moisture deficiency may occur even with a positive yearly runoff, due to evaporation during the growing season (e.g. the summer) if the precipitation is relatively low. If precipitation - during the growing season - is at a minimum while evaporation is at a maximum, they are "out of phase". A soil moisture deficiency can be matched by irrigation, a surplus by drainage.

Table 1.4. Climate, vegetation and soil type

	ZONE, LATITUDE	PRECIPITA- TION M/YEAR (ROUNDED)	EVAPORATION	VEGETATION TYPE	SOIL TYPE
(sub) arctic	tundra, 65 - 75°	< 0.5	-	tundra	(tundra)
	continental subarctic, 50 - 70°	< 0.5	-	needle leaf forest, taiga	podzol
middle lati- tude	humid - marine 40 - 60°	1.0 - 2.0	$P > E_p$, out of phase	needle leaf forest, summer green forest	podzol
	- continental	0.5 - 1.0	$P \geq E_p$, in phase	summer green forest	gray-brown podzol
	arid - steppe* 35 - 50°	0.25 - 0.5	$P < E_p$	grasses, shrubs	reddish soil, caliche
	- desert**	< 0.25			
sub- tropic	Mediterranean 30 - 45°	0.3 - 0.75 (dry summer)	$P < E_p$, out of phase	sclerophyll forest, shrubs	reddish-brown soil, terra rossa
	sub-humid 30 - 55°	< 1.0 (dry winter)	$P \approx E_p$, in phase	pampa, prairie	chernozem
	humid*** 25 - 25°	1.0 - 1.5	$P > E_p$	temperate rainforest	red-yellow soil, latosol
	arid - steppe 15 - 35° - desert	< 0.25	$P \ll E_p$	(steppe-desert)	brown-chestnut soil, salt, CaCO_3 , reddish soil
equato- rial	wet - dry 5-25°	1.0 - 2.0 (monsoon)	$P \approx E_p$, in phase	savanna	red-yellow soil, latosol
	wet 10°N - 10°S	> 2.0	$P \gg E_p$, in phase	rainforest	latosol

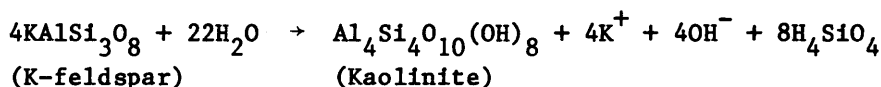
* Pueblo type, ** Gobi type, *** China-Florida type

1.2.3. The soil

Chemical weathering

Rainwater which infiltrates with its dissolved oxygen, carbonic acid and inorganic and organic acids is the main agent in chemical weathering. The very slow reaction rates cause alterations that are only partly complete. Keeping this in mind, the following chemical processes take place during chemical weathering:

- oxidation, e.g. of iron, manganese and sulphur
- dissolution, e.g. of carbonates, silica
- hydration, e.g. of oxides of iron ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ called "limonite", mainly fine grained Goethite α - FeOOH) and of aluminum ($\text{Al}(\text{OH})_3$, Gibbsite)
- hydrolysis, which is dissolution and formation of acids and bases, e.g. the weathering of feldspar to clay minerals. A simplified formula is as follows:



The solute becomes alkaline (basic) as alkali and alkaline-earth metals dissolve.

In warm-humid climates the clay mineral Kaolinite predominates, and in semi-arid climates, the clay minerals

Montmorillonite $(\text{Al}, \text{Mg}, \text{Fe}^{3+})_4 (\text{Si}, \text{Al})_8 \text{O}_{20} (\text{OH})_4 \cdot n\text{H}_2\text{O}$
and Illite $\text{K}_{0-2} (\text{Al}, \text{Mg}, \text{Fe}^{3+})_4 (\text{Si}_{8-6}, \text{Al}_{0-2}) \text{O}_{20} (\text{OH})_4$ dominate.

We must keep in mind that, with irrigation, the composition and physical characteristics of clay minerals could be changed.

Soil-physical characteristics

For our purpose two important processes have to be reminded, the ion exchange and the flocculation of colloids.

The substitution of Al^{3+} for Si^{4+} and of Mg^{2+} for Al^{3+} in Montmorillonite and Illite crystal layers leaves a deficiency in positive charges. The deficiency may be compensated by adsorbed cations which are readily replaced by other cations (CEC, cation exchange capacity). Because of the high specific surface (area per unit mass, for e.g. Montmorillonite about $750 \text{ m}^2/\text{g}$) the CEC amounts to about 0.1 mequiv/g for Kaolinite to 1.5 mequiv/g for Montmorillonite. The CEC may be pH-dependant (Baver, Gardner, Gardner, 1972; Greenland & Hayes, 1981), CEC may increase with increased pH. At lower pH values, Kaolinite may especially exhibit positive charges by uptake of H^+ and consequently may adsorb anions (AEC about 0.4 mequiv/g). Cl^- and SO_4^{2-} ions are only weakly adsorbed at low pH, phosphate ions strongly. PO_4^{3-} forms also insoluble compounds with hydrous iron and aluminum oxides in the soil. Adsorption depends on the radius and the charge of the hydrated ions giving the "lyotropic" series $\text{Cs} > \text{Rb} > \text{K} \approx \text{NH}_4 > \text{H}_3\text{O}^+ > \text{Na} > \text{Li}$, with Li the weaker adsorbed. There are exceptions however for different minerals. The divalent cations are stronger adsorbed ($\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$), and trivalent Al, Fe ions still more than the bivalent ions. The relation between the amount of substance adsorbed to the concentration in solution is known as the adsorption isotherm. The Langmuir adsorption equation reads as follows. A fraction θ of the fixed number of adsorption sites is occupied by adsorbed particles. The rate of desorption is equal to $k_d \theta$, k_d is constant at constant T. The rate of sorption is $k_a(1 - \theta)C$, with C as concentration of particles per m^3 . The number $k_a/k_d = b$ is called the adsorption coefficient.

It follows that at equilibrium $\theta = bc / (1 + bc)$

Sometimes the Freundlich isotherm is more useful:

$$\theta = K.C^{1/m}, m > 1, K \text{ a constant.}$$

Under influence of their electric charge, the clay particles may "dissolve" as colloids, repelling each other with their negative surfaces. Both the clay particles and the exchangeable bases (cations) are hydrated which causes a higher dispersion. A salt solute may diminish the repellent force occurring between the clay particles, and they may consequently flocculate. A flocculated clay is more permeable to water than a dispersed one. A low salt concentration, together with predominance of sodium as exchangeable cation, disperses clay particles, causing deterioration of soil structure and diminishing of the permeability. Colloidal organic matter in the soil reacts much in the same way as the clay minerals with respect to ion exchange and formation of stable soil aggregates. Ca and Fe cause humic acids to be precipitated on the surface of the clay.

Soil-forming processes

The soil in which the vegetation roots itself is formed in the more or less weathered rock (regolith) under strong biological influence. There exists an interaction between climate (temperature, humidity), soil (physical and chemical properties) and the biological activity (microbial life, vegetation etc.). See also table 1.4.

1. With shallows stagnant or upward seeping saturated (not saline) groundwater, gleization takes place. The high groundwater level causes a reduced environment characterized by bluish, ferrous iron compounds. Mostly in cool climates, bogs.

2. With continuous downward seepage (annual precipitation excess) and an oxygen-rich unsaturated zone, podzolization takes place with a leached upper (A) layer and an enriched lower (B) layer. In the A layer, the exchangeable cations ("bases" Na^+ , K^+ , Ca^{2+} , Mg^{2+}) adsorbed to the clay minerals are replaced by hydrogen, making the soil rather acid. In the B layer clay-humus colloids and oxides of iron and aluminum which connect humus and clay particles to each other, precipitate. In moist-warm climates, the clay minerals are

further decomposed to Gibbsite and silica, the latter being leached out (laterization, giving neutral latosols).

3. With continuous capillary rise and evaporation in (semi-) arid climates calcification takes place (caliche formation). Mg^{2+} and Ca^{2+} ions remain in the soil and colloids are flocculated. In desert climates salinization is created (alkaline soils)

4. At low temperature, bacterial activity is low and humus is accumulated.

5. At high temperature no humus is formed, due to high bacterial activity.

Remark: Some rocks give special soils which do not fit in the system. Lime rich parent materials originate e.g. the rendzina.

1.3. THE BIOTIC SUBSYSTEM

1.3.1. The trophic system

Food chains

For the description of the ecological structure of a biotic community the following terms are useful.

We distinguish:

- autotrophs (self-nourishing organisms) or producers which manufacture food from simple inorganic substances: mainly green plants,
- heterotrophs (other-nourishing organisms),
 - a. macro-consumers (phagotrophs): grazers (herbivores) and carnivores,
 - b. micro-consumers (saprotrophs): decomposers like bacteria, fungi, yeasts, molds, protozoa.

These are interconnected by food chains, e.g. autotrophs → herbivores → carnivores → saprotrophs. The trophic levels can be described as reservoirs (with as unit: individual living beings, kg biomass or J energy) with their proper fluxes. The biomass of terrestrial plants is 18.8 kJ per g dry weight or about 8.5 kJ per g wet weight, the total biomass (standing crop) could for example be 0.5 kg dry weight per m² for grassland or 10 kg/m² for forest (table 1.5.).

Table 1.5. Biomass B and net yearly primary production P_n of some vegetations (Larcher 1976, Collinson 1977).

CLIMATIC ZONE	DRY MATTER, IN TON PER HA.	
	B	P_n
tundra	0,1 - 20	0 - 4
summergreen forest	200 - 400	4 - 25
prairie	20 - 50	2 - 10
savanna	60 - 100	5 - 35
rain forest	400 - 500	10 - 35

Bacterial processes which provide nutrients to higher plants can be quite important in the soil which can have about 10^8 bacteria per g soil or 10 to 100 g biomass per m^2 . Seasonal changes in numbers of bacteria are closely related to fluctuations in moisture and temperature. The greatest number of bacteria is found in the uppermost say 10 cm of the soil, in organic soils often in the uppermost meter. The same holds for fungi, which have an abundance of 50 to 500 g biomass per m^2 (Alexander, 1977).

Energy flows

The energy flow can be symbolized as follows. Of the global radiation (par. 1.2.1.) ($S_b + S_d$), the solar radiant energy on a yearly base, a maximum of 50% (the visible part) is absorbed by autotrophs. Only 5% (maximum) to 0.2% (average biosphere) of ($S_b + S_d$) is used for gross primary production (P_g), and only 4% (maximum) to 0.1% (average biosphere) of the solar radiant energy is available to heterotrophs (set equal to the net primary production P_n). With R as respiration of the plants, $P_n = P_g - R$, R is about 30% of P_g .

For harvesting only the net community production P_{nc} is available, that is P_n minus consumption by heterotrophs. Agriculture aims at maximizing the net community production by putting energy in cultivation, irrigation, fertilizing and insect control. Odum (1971) gives for P_{nc} the following figures: alfalfa (U.S.A.): 60.5×10^6 J/m² per year; temperate forest: 8.4×10^6 J/m² per year; mature rain forest; little or none. However P_g is as follows: alfalfa (U.S.A.): 102.5×10^6 J/m² per year, temperate forest 48.3×10^6 J/m² per year and mature rain forest 189×10^6 J/m² per year. Cultivated lands with little energy subsidy have a P_g of about 12.6×10^6 J/m² per year. Odum estimates the terrestrial P_g at 241×10^{16} kJ per year for the whole biosphere of 135.0×10^6 km².

1.3.2. Limiting factors

Growth rate and limiting factors

The growth rate or "Blackman" curves for crops can be described as:

$$(1 - q/Ax) (1 - q/By) (1 -) \dots (1 - q/Q) = Z, \quad 0 < Z < 1$$

A,B ... are the slopes of the graphs for the yield q in kg.ha⁻¹.d⁻¹ versus the (limiting) growth factor $x,y \dots$ Q is the maximum possible yield. The most important limiting factors for crop growth are (soil)air, light, temperature, water and nutrients.

Air

The composition of free air can be taken as constant (0.03 vol % CO₂) but that is not true in the soil where the CO₂ vol% can be 10 to 100 times higher because of "soil respiration" by roots or microbes. In temperate climates about $100 \text{ kg.ha}^{-1}.\text{d}^{-1}$ CO₂ are produced during summer (Alexander, 1977).

A percentage of 3 to 5 % CO_2 is toxic for roots of arable crops. Oxygen may thus become a limiting factor in the soil for rootgrowth and moreover the lowered reduction potential causes the dissolution of toxic heavy metals.

Light

Light is the main factor for photosynthesis. The CO_2 that is required must pass through the stomata which normally open under influence of light. Under optimal circumstances brutto photosynthesis or gross primary production P_g can reach - depending on temperature - 50 kg (temperate zone) to 100 kg (tropical crops) $[\text{CH}_2\text{O}]_n$ per ha per hour. For example, during the growing season in the Netherlands with a mean daily temperature above 10°C , which lasts from mid April to mid October, the theoretical maximum harvested dry matter yield of crops is $3/4 P_n$ or $200 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{d}^{-1}$ or $30.000 \text{ kg} \cdot \text{ha}^{-1}$ over a climatologically normal season (De Wit, 1965). In practice the yield is much lower because of limiting factors but hay yields of 20 t dry matter have been reached in the Netherlands.

Temperature

The influence of temperature causes, according to the Arrhenius Law, a doubling of reaction rates with ΔT of about 10 K. Below an optimum temperature, the same holds for biochemical reactions. Examples are the "dark"reaction of photosynthesis, respiration and bacterial activity (nitrification, N_2 fixation etc.).

Water

Besides plant nutrients, water is the most important limiting factor that can be influenced by man. Plant evaporation can be described as a physical process (par. 1.2.1.) with the stomata as main regulators. The physiology of the stomata is quite complicated (influence of $[\text{K}^+]$, hormones, photosynthesis). In general, they close under

stress circumstances, e.g. lack of soil water, high temperatures or high vapour pressure deficits, thus protecting the plant from drying out. When opened, stomatal resistances of several crops amount to 1 to 2 s/cm (Monteith, 1975). This is of the same order as r_E of air at low wind velocities (par. 1.2.1.).

The mechanisms of plant evaporation E_A and net photosynthesis P_n go partly parallel, they are both influenced by stomatal resistance, radiation and temperature. Therefore, between limits,

$$P_n = \text{const.} (E_A/E_p) \text{ kg.ha}^{-1}.$$

The efficiency of water use by crops is higher at higher nutrient levels. In the Netherlands with yearly hay yields of 10 t.ha⁻¹ dry matter, the marginal efficiency was 15 kg.ha⁻¹.mm⁻¹ and with 18 ton 50 kg.ha⁻¹.mm⁻¹ (Van Boheemen, 1980). For spring wheat a marginal efficiency of 33 kg.ha⁻¹.mm⁻¹ (incl. 12 kg.ha⁻¹.mm⁻¹ grain) of dry matter was reached with a nitrogen dressing of 100 kg.ha⁻¹ in surplus of 50 kg N per ha which was delivered by the soil (Hellings, 1980).

At high temperatures, P_n does not increase any more but E_A does, which results in inefficient use of water (e.g. irrigation water) which is then mainly used by the plant for cooling. At soil water suctions higher than field capacity, E_A diminishes in % more than P_n - until the wilting point is reached (Fig. 1.3.).

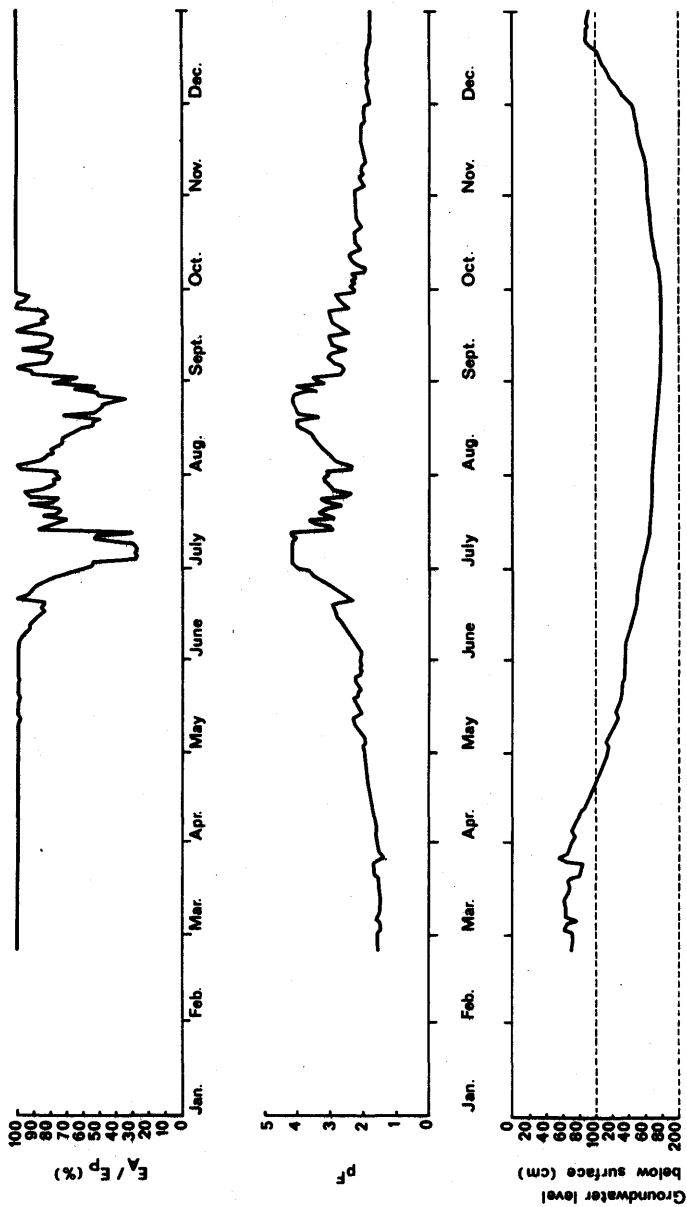
Nutrients

Nitrogen, phosphorus and potassium are among the most important fertilizers which aim at preventing N,P and K to become limiting factors.

The fate of fertilizers, manures and litter depends on

- uptake by plants,
- activity of microorganisms,
- fixation, sorption and leaching.

All these processes are interconnected.



Hupsel, Netherlands 1976

Fig. 1.3. Reduction of relative evapotranspiration of grassland E_A / E_P due to soil water depletion in 1976. Medium fine sand. ^A_P
(Experimental station Hupsel, Netherlands)

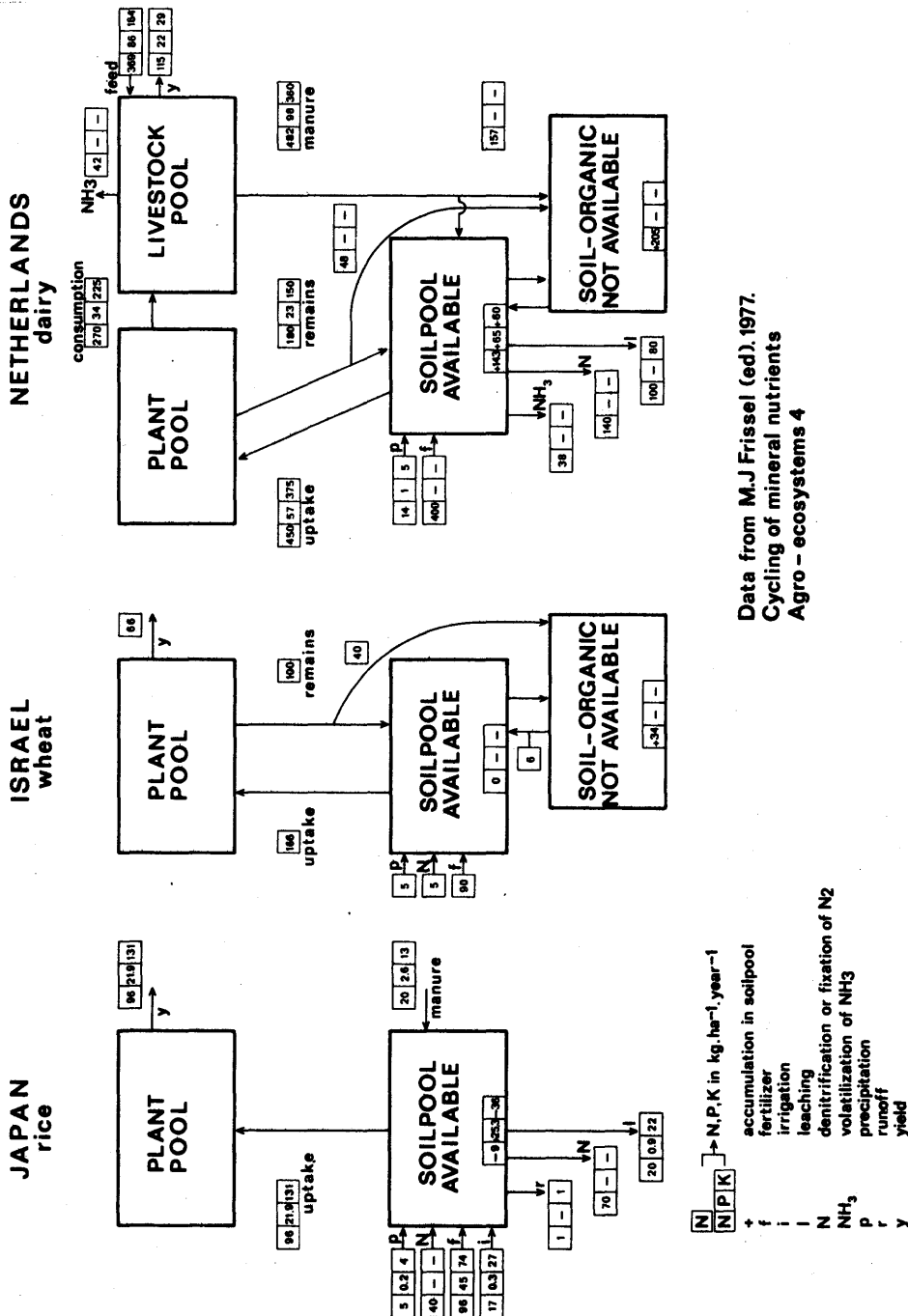
Plant uptake is best known from analysis of the harvest. Cooke (1975) gives the following figures.

Table 1.6. Amounts of major nutrients (kg/ha) in average yields (Cooke, 1975).

YIELD t.ha ⁻¹		kg.ha ⁻¹						ANALYSIS OF
		N	K	Ca	Mg	P	S	
wheat	4 grain	80	40	10	5	12	20	grain + straw grain + straw roots + tops grains
barley	4 grain	70	30	10	5	12	15	
sugar beet	40 fresh root	230	220	70	25	20	30	
beans	2.5 grain	110	50	20	5	15	25	
kale	50 fresh crop	200	180	200	20	25	100	
grass	10 dry crop	250	250	70	20	30	15	
clover	5 dry crop	150	100	100	10	10	10	tubers
potatoes	50 tubers	180	200	10	15	25	20	
lucerne	10 dry crop	280	180	250	20	30	30	

The ions taken up must be electrically balanced, so if K^+ is taken up, it is exchanged against e.g. H^+ . In the same way NO_3^- or HPO_4^{2-} taken up can be exchanged against HCO_3^- etc. (Amberger, 1979). Uptake by roots will be optimal if both oxygen is present for root respiration and soil water is available for nutrient transport (massflow or diffusion).

Microorganisms play a decisive role in nutrient cycles. As micro-consumers they metabolize litter and other organic remains and release inorganic ions during decomposition (mineralization) which are useful to autotrophs. Some bacteria may oxidize H_2S or NH_3 (aerobic respiration). These biochemical reactions influence the reduction potential and the acidity of the soil environment. Bacterial activity, e.g. mineralization is governed by factors like aeration, temperature (optimum 30 à 40°C), soil water content (optimum at field capacity), acidity (optimum neutral pH), additional carbohydrates, and clay content which hems mineralization by adsorption of e.g. enzymes.



Data from M.J Frissel (ed). 1977.
Cycling of mineral nutrients
Agro - ecosystems 4

Fig. 1.4. Nutrient cycles for nitrogen, phosphorus and potassium.
Japan: paddy rice. Grain yield 4560 kg/ha per year. Irrigation 15,000 m³/ha per year.
Israel: wheat, straw returned. Grain yield 3500 to 4500 kg/ha per year. Semi-arid climate.
Netherlands: dairy farm, 4 milkcows plus 4 calves per ha. Yield 18,000 kg/ha per year milk and 770 kg/ha per year meat. Sandy soil. Temperate climate.

The nitrogen balance in soil can be symbolized as follows (N_1 is inorganic nitrogen):

$\Delta N_1 = N_m - (N_a + N_p + N_l + N_d)$, with as suffixes m = mineralized, a = assimilated by microflora, p = plant uptake, l = leached, d = volatilized by denitrification or urea bacteria.

Nitrification of NH_4^+ to NO_3^- which leaches is retarded by the clay humus complex because of adsorption of NH_4^+ . Especially high amounts of NO_3^- become available in freshly ploughed grassland (200 to 300 kg N/ha.year). Volatilization of urea can be as high as 70%. Nitrate respiration ($\rightarrow \text{N}_2, \text{N}_2\text{O}, \text{NO}$) requires neutral pH and anaerobic environment (Fig. 1.4.). In the same way, microorganisms cause through mineralization leaching of SO_4^{2-} and under anaerobic conditions losses by producing H_2S and organic sulphur compounds.

Fixation and sorption are most important for K and P_1 (inorganic phosphate). In a single year not more than 1/4 or 1/3 of the side dressing of P_1 fertilizer will reach plant roots (Cooke, 1975). This is however a short-term disadvantage, large reserves of fixed P and K can supply future crops.

Soluble salts like NO_3^- , SO_4^{2-} , Cl^- , Na^+ , Ca^{2+} , Mg^{2+} will be leached, depending on the dressings and rainfall. Cooke (1975) mentioned for the U.K. losses of 150 kg/ha.year of Ca, 5 - 30 kg Mg/ha.year and 1/4 of the applied N in case of intensive agriculture. Amberger (1979) mentions for lysimeters in the F.R.G.: 300 to 400 kg Ca/ha.year, 70 - 90 kg Mg/ha.year and about 20 kg K/ha.year as losses due to leaching. Optimal N dressings with respect to dry matter yield are in temperate climates for wheat about 150 kg/ha.year and for grass 400 to 500 kg N/ha.year (of course if the other nutrients are not limiting).

List of symbols

TERM	SYMBOL	UNIT
biomass	B	kg.m^{-2}
molar concentration of A	$c_A, [A]$	mol.m^{-3}
concentration of A	$C_A, [A]$	g.m^{-3}
specific heat, constant pressure	c_p	$\text{J.kg}^{-1}.\text{K}^{-1*}$
vapour pressure	e	mbar
saturation vapour pressure	e_s	mbar
cumulative evaporation	E	mm
id. actual	E_A	mm
id. "open water" - Penman	E_o	mm
id. potential	E_p	mm
evaporation fluxdensity	E_m	$\text{kg.m}^{-2}.\text{s}^{-1}$
advection	ΔF	W.m^{-2}
soil heat fluxdensity	G	W.m^{-2}
sensible heat fluxdensity	H	W.m^{-2}
terrestrial radiation fluxdensity	L	W.m^{-2}
id. downward	L_d	W.m^{-2}
id. net	L_n	W.m^{-2}
id. upward	L_u	W.m^{-2}
latent heat of vaporization	$L (2.47 \times 10^6)$	J.kg^{-1}
evaporation heat fluxdensity	LE_m	W.m^{-2}
snowmelt heat fluxdensity	M	W.m^{-2}
pressure	p	$\text{Pa} = 10^{-5} \text{bar}$
precipitation depth	P	mm
gross primary production	P_g	$\text{kg.m}^{-2}.\text{s}^{-1}$
net primary production	P_n	$\text{kg.m}^{-2}.\text{s}^{-1}$
net community production	P_{nc}	$\text{kg.m}^{-2}.\text{s}^{-1}$

* also $\text{J.mol}^{-1}.\text{K}^{-1}$. For dry air $c_p = 1.0 \times 10^3 \text{ J.kg}^{-1}.\text{K}^{-1}$

TERM	SYMBOL	UNIT
albedo	r	-
diffusion resistance	r	$m^{-1}.s$
id. canopy	r_c	$m^{-1}.s$
id. vapour	r_E	$m^{-1}.s$
id. stomatal	r_s	$m^{-1}.s$
respiration	R	$kg.m^{-2}.s^{-1}$
net radiation fluxdensity	R_n	$W.m^{-2}$
slope of saturation vapour pressure at air temperature	s	$mbar.K^{-1}$
solar constant	S_o (1.39)	$kW.m^{-2}$
solar radiation fluxdensity	S	$W.m^{-2}$
id. direct beam	S_b	$W.m^{-2}$
id. diffuse	S_d	$W.m^{-2}$
id. net	S_n	$W.m^{-2}$
absolute temperature	T	K
horizontal wind velocity	u	$m.s^{-1}$
runoff depth	U	mm
Bowen ratio	β	-
psychrometric constant	γ	$mbar.K^{-1}$
density	ρ	$kg.m^{-3}$
density of moist air	ρ_m	$kg.m^{-3}$

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2. MOVEMENT OF AGROCHEMICALS IN THE UNSATURATED AND SATURATED ZONES

V. BENEŠ

2.1. MOVEMENT OF AGROCHEMICALS IN THE UNSATURATED ZONE

The basic factor affecting the movement of agrochemicals in the unsaturated zone is the flow of groundwater in its liquid state. The role of water vapour and air in the transport processes is very small. Movement of a solute in water is affected by the following interactive processes:

a) Convection

The movement of a solute is at the same rate and in the same direction as the groundwater flow. This movement is, especially with substances which are inert and do not react with soil, dominant and some studies do not consider any other influences.

b) Hydrodynamical dispersion

This process is a combination of molecular diffusion and mechanical dispersion (Fig. 2.1).

c) Hydrochemical interactions

These occur between the solute, water, soil complex, the vegetation root system and the microbiological system.

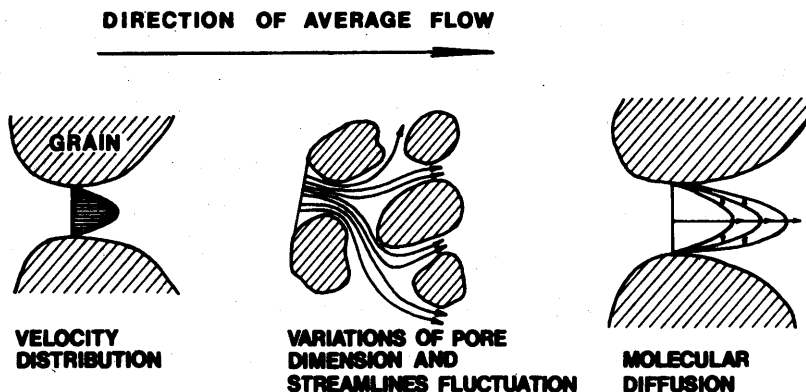


Fig.2.1. Spreading due to mechanical dispersion and molecular diffusion (after Bear, 1979)

The influence of individual processes is illustrated in figure 2.2. with characteristic break-through curves. Changes in concentration are drawn for a one-dimensional system of movement of matter.

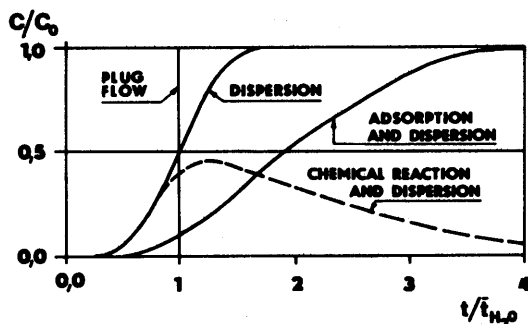


Fig.2.2. Characteristic breakthrough curves for non-reactive, reactive and adsorption contaminant (after Roberts et al. 1980).

The ideal plug flow occurs in the case of the purely convective movement of the substance. From the response curve of the relative concentration of a tracing element for dispersive flow it is obvious that particles of solute are retarded or accelerated in relation to the mean rate of water flow. The influence of the reversible adsorption process and of geochemical reactions of the movement is clearly illustrated by the respective curves in figure 2.2.

Movement of agrochemicals in the unsaturated zone is usually considered to be a one-dimensional process namely in the vertical direction.

2.1.1. Water in the unsaturated zone

The amount of water in the unsaturated zone or soil water content is defined as:

gravimetric water content - the ratio of water mass and soil mass

$$w = m_w / m_z = \rho_w V_w / (\rho_s V_s - \rho_w V_w) \quad (2.1)$$

The symbol m_z denotes the mass of dehydrated soil at a temperature of 105°C

volumetric water content - the ratio of water volume and soil sample volume

$$\Theta = V_w / V_s \quad 0 \leq \Theta \leq n \quad (2.2)$$

water saturation - the ratio of water volume and the total volume of pores

$$S_w = V_w / V_p \quad 0 \leq S_w \leq 1 \quad (2.3)$$

The relationship between the gravimetric and volumetric water content is given by

$$\Theta = (\rho_s / \rho_w) w / (1 + w) \quad (2.4)$$

The relationship between volumetric water content and water saturation is given by

$$\Theta = S_w \cdot n \quad \text{Where } n = (V_p / V_s) \quad (2.5)$$

Methods of soil water content measuring

a) Gravimetric method

The mass of soil sample before and after dehydration (at 105°C) is determined. The difference between the two values is the mass of water in the soil.

b) Electric resistance method

Electrical conductivity of soil increases with increasing soil water content.

c) Electric capacity method

The capacity of the condensator formed by two electrodes with soil as dielectric between them depends on soil water content.

d) Gamma ray method

Absorption of radiation is directly proportional to the mass of the irradiated sample and thus to the soil water content.

e) Neutron method

In the course of fast neutron interaction with nuclei of atoms of small atomic mass, the fast neutrons are decelerated. The strongest moderators are hydrogen atoms. The content of hydrogen in the crystal grid of solid is relatively small and the modulation effect will depend predominantly on soil water content.

2.1.2. Water flow in the unsaturated zone

Assume an inhomogeneous, nondeformable porous medium, in which movement of water in its vapour phase is not considered, and in which influence of the gradient of salts concentration (osmotic effect) and of temperature changes (thermo-osmotic effect) on the groundwater potential are neglected. The one-dimensional vertical flow in that case can be described by two fundamental equations:

Darcy's law

$$v = -K(z) \left(\frac{\partial H}{\partial z} \right) \quad (2.6)$$

The total hydraulic potential H can be expressed as the sum of the soil water potential h and the gravity potential z .

$$H = h + z \quad (2.7)$$

Substituting equation (2.7) into equation (2.6) and assuming the Z -axis is zero on the soil surface and positive Z -values are in the downward direction, the following relation for the flow rate is obtained:

$$v = -K(z) \left[\left(\frac{\partial h}{\partial z} \right) - 1 \right] \quad (2.8)$$

Equation of continuity

$$\frac{\partial \theta}{\partial t} = - \frac{\partial v}{\partial z} \quad (2.9)$$

Using the fundamental equations (2.8) and 2.9) a relation can be derived, describing unsteady flow in the unsaturated zone:

$$\frac{\partial \theta}{\partial t} = \left(\frac{\partial}{\partial z} \right) \left[K(z) \left(\frac{\partial h}{\partial z} - 1 \right) \right] \quad (2.10)$$

Equation (2.10) is non-linear, values $K(z)$ and h depend on the soil water content θ . In order to eliminate the problem of two dependent variables θ and h the expression $c(h) = \frac{\partial \theta}{\partial h}$ is substituted into the equation (2.10) where $c(h)$ is the differential soil water capacity.

$$\frac{\partial \theta}{\partial t} = \left(\frac{\partial \theta}{\partial h} \right) \left(\frac{\partial h}{\partial t} \right) = c(h) \left(\frac{\partial h}{\partial t} \right) \quad (2.11)$$

Equation (2.10) can be rearranged as follows

$$\frac{\partial h}{\partial t} = (1/c(h)) \left(\frac{\partial}{\partial z} \right) \left[K(z) \left(\frac{\partial h}{\partial z} - 1 \right) \right] \quad (2.12)$$

Equation (2.12) can be rewritten in the diffusion form by introducing the coefficient of soil water diffusivity:

$$D(\theta) = K(z) \left(\frac{\partial h}{\partial \theta} \right) \quad (2.13)$$

The diffusion form of the equation of flow is

$$\partial \theta / \partial t = (\partial / \partial z) [D(\theta) (\partial \theta / \partial z)] - \partial K(z) / \partial z \quad (2.14)$$

Water flow in the active root zone

In order to describe water flow in the active root zone, i.e. in the layer of soil which contains the vegetation root system, equation (2.12) is supplemented by expression $A(z,t)$ representing the uptake of water by plant roots varying in time and space.

$$\partial h / \partial t = (1/c(h)) (\partial / \partial z) [K(z) (\partial h / \partial z - 1)] - A(z,t)/c(h) \quad (2.15)$$

2.1.3. Soil water potential

The soil water potential or pressure head depends on the soil physical properties S (i.e., grain surface, grain shape etc.), soil water content θ , soil temperature T and on the history of wetting and drying R .

Milly and Eagleson (1980) introduce a general relation for the water potential:

$$h = h(S, \theta, T, R) \quad (2.16)$$

The water potential dependence on individual parameters described by equation (2.16) cannot be used for practical purposes. The influence of some of the parameters in equation (2.16) cannot easily be determined by field measurements or laboratory tests on undisturbed soil samples.

For practical calculations of water flow in the unsaturated zone the influence of temperature and the history of wetting and drying are usually ignored.

Soil water potential is expressed by various empirical relations that only take into consideration the influence of soil water content and soil characteristics.

Selim and Iskandar (1980) give the relation

$$\theta(h) = \theta_s / [1 + (-h/a)^b] \quad (2.17)$$

Parameters a and b depend on the type of soil. Mualem (1976) introduces dimensionless water content

$$\Xi = (\theta - \theta_r) / (\theta_s - \theta_r) \quad (2.18)$$

The soil water potential dependence on the dimensionless water content is then expressed by

$$\Xi = [1 / (1 + (\alpha h)^n)]^m \quad (2.19)$$

Van Genuchten (1978) gives calculated relations of soil water potential versus water content for various soil types according to equations (2.18) and (2.19) (shown in Fig. 2.3.).

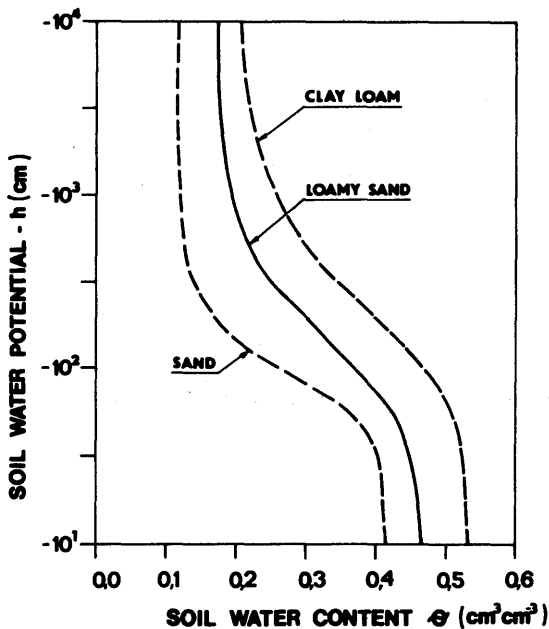


Fig.2.3. Retention curves for various soil types calculated from equation 2.19 (after van Genuchten, 1978)

Tanija et al. (1981) express the relation of soil water potential vs. soil water content by a simple regression equation:

$$\theta(h) = b_0 + b_1 \log h + b_2 (\log h)^2 \quad (2.20)$$

The soil water potential can generally acquire a wide range of values and due to this fact the semilogarithmic form is generally used for expressing this relationship.

This relation is called the pF-curve or the retention curve:

$$pF = \log | -h |$$

Figure 2.4. illustrates the characteristic shape of the pF-curves and the influence of soil type and structure.

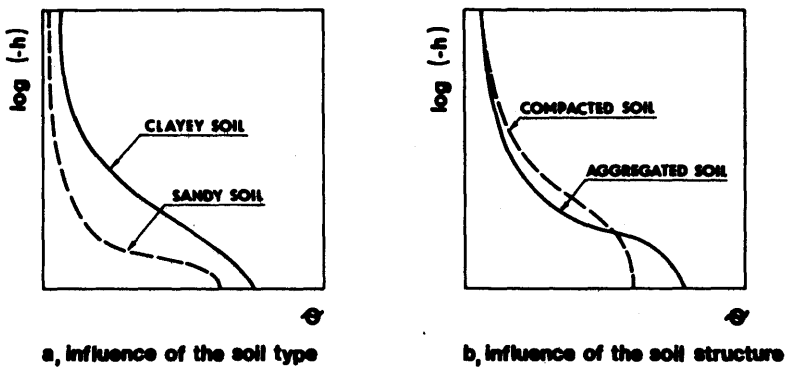


Fig.2.4. Influence of soil properties on the shape of the retention curve (after Hillel, 1971).

Hysteresis appears in the relation of the soil water potential vs. soil water content. The soil water potential is affected by the history of wetting and drying of soil (Fig. 2.6.).

Several factors cause hysteresis. The first, called "the ink-bottle effect" (Fig. 2.5a), results from the fact that as water reenters narrow channels, a local increase of suction is required. In the soil at this stage we have instability and the interface cannot advance until a neighboring pore is filled. Equilibrium at a given suction may be obtained with somewhat different θ .

The second effect, sometimes called "the raindrop effect" (Fig. 2.5b), is due to the fact that the contact angle at an advancing interface differs from that at a receding one.

Entrapped air is another factor causing hysteresis. Milly and Eagleson (1980), Mualem (1976), van Genuchten (1980) treat this problem in fuller detail.

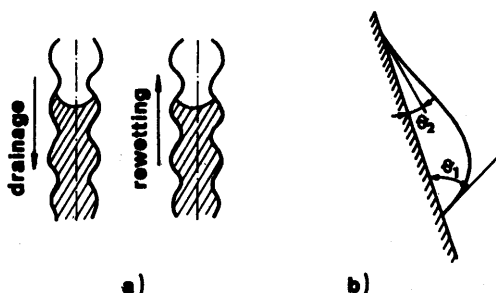
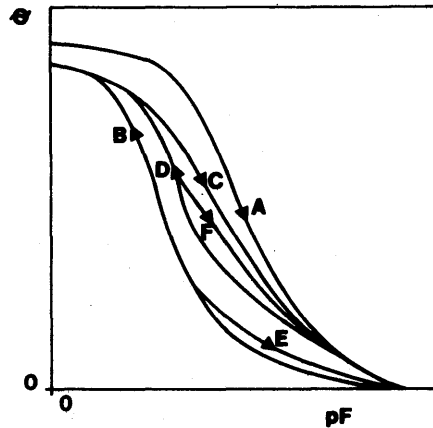


Fig.2.5. Factors causing hysteresis in retention curve (after Bear, 1979).

- a) The "ink-bottle" effect
- b) The "raindrop" effect



- A - FIRST DRYING CURVE
- B - MAIN WETTING CURVE
- C - MAIN DRYING CURVE
- D - PRIMARY WETTING CURVE
- E - PRIMARY DRYING CURVE
- F - SECONDARY DRYING CURVE

Fig.2.6. Hysteresis of the retention curves (after Milly and Eagleson, 1980)

Methods for measuring soil water potential - pF curves

There are mainly two methods for measuring soil water potential:

a) Laboratory measurements on undisturbed soil samples

The measurements are usually carried out for the drying (draining) part of the retention curve. The sample of soil is placed into the measuring apparatus (while hydraulic continuity between the soil sample and the reference level of free water is maintained). The soil sample is dried either by air pressure above the sample, or by water suction under the sample. Figure 2.7. illustrates schematically the principle of both types of apparatus.

b) Field measurements

Measurements are carried out with the help of a tensiometer sunk to a required depth in the soil profile. The principal part of a tensiometer consists of a porous vessel - the sensor, which achieves hydraulic connection between soil water and a manometer. Figure 2.7a shows schematically a tensiometer with a mercury manometer. For practical purposes the mercury manometer is replaced by a pressure recorder. For measuring high values of the potential, of the order of $10^4 - 10^6$, soil potential psychrometers (psychrometric microvoltmeters) are intended. These devices operation is based on the balanced relation between soil water content and relative humidity of air. In any case, however, coefficients of the relevant relation should be determined by experimental measurements.

When evaluating experimental results it is useful to choose an appropriate empirical formula.

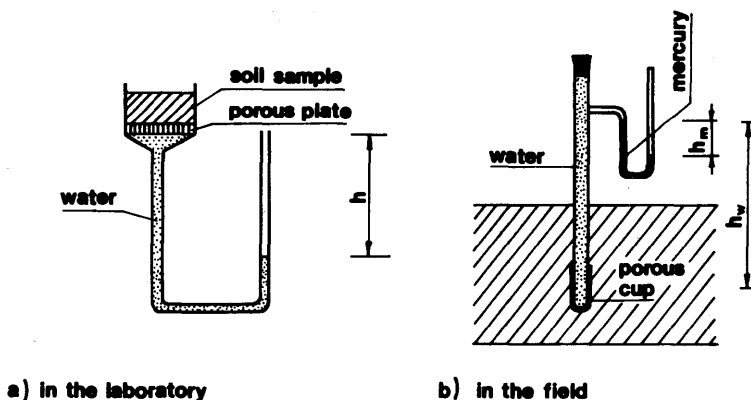


Fig.2.7. Measurement of soil water potential

a) in the laboratory

b) in the field

2.1.4. Hydraulic conductivity

Hydraulic conductivity for water flow in the unsaturated zone is not a constant value dependent on soil characteristics only, as it is in the case of the saturated zone. Hydraulic conductivity depends on the same factors as the soil water potential (see equation 2.16). Assuming isothermal flow and neglecting hysteresis (these assumptions are made in most practical calculations of water flow), various empirical relations of hydraulic conductivity vs. soil water content or soil water potential or soil characteristics are given in the literature. The relation of hydraulic conductivity vs. soil water content is given by Tanija et al. (1981) as follows:

$$K(\theta) = K_0 \exp \beta (\theta - \theta_0) \quad (2.21)$$

Selim (1980) uses the simpler Gardner formula:

$$K(\theta) = n \exp(\alpha \theta) \quad (2.22)$$

Van Genuchten based his expression for hydraulic conductivity on Mualem's equations for the soil water potential (formulas (2.18) and (2.19)) and obtained the following expressions:

a) dependence on soil content:

$$K(\theta) = K_0 \theta^{\frac{1}{2}} [1 - (1 - \theta^{1/m})^m]^2 \quad (2.23)$$

b) dependence on soil water potential

$$K(h) = \{1 - (\alpha h)^{n-1} + [1 + (\alpha h)^n]^{-m}\}^2 K_0 / [1 + (\alpha h)^n]^{m/2} \quad (2.24)$$

Since experimental determination of coefficients of hydraulic conductivity under conditions of flow in the unsaturated zone is difficult, Mualem's equations (2.23) and (2.24) are very practical. Relations for $K(h)$ or $K(\theta)$ can be determined with the help of parameters established for the retention curves. The empirical relation calculated for various soil types is plotted in figure 2.8.

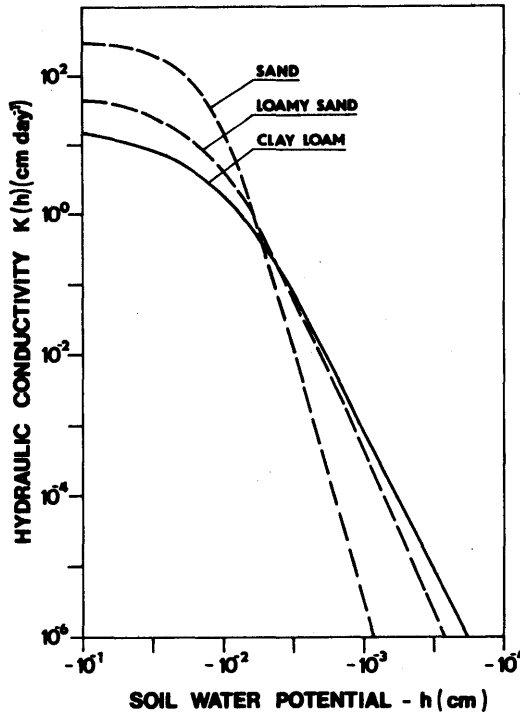


Fig.2.8. $K(h)$ vs h plotted according to equation 2.24 (after van Genuchten, 1978)

Rijtema (1965) recognizes different types of formulas expressing the relation of hydraulic conductivity vs. soil water potential dependent upon the soil water potential value:

$$K(h) = K_0 \quad \text{for } h \geq h_a \quad (2.25)$$

$$K(h) = K_0 \exp \left[(h-h_a)\alpha \right] \quad \text{for } h_a \geq h \geq h_{lim} \quad (2.26)$$

$$K(h) = a(-h)^{-n} \quad \text{for } h < h_{lim} \quad (2.27)$$

Formulas given by equations (25) - (27) are plotted in figure 2.9.

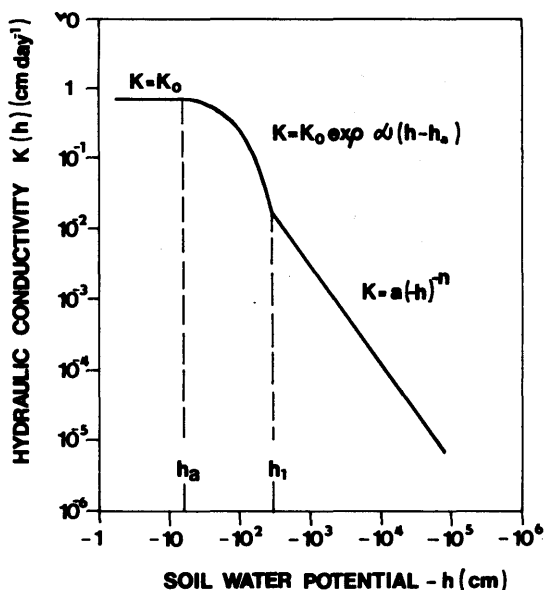


Fig.2.9. Hydraulic conductivity vs soil water potential plotted according to equations 2.25 - 2.27 (after Rijtema, 1965)

To describe experimentally determined values of hydraulic conductivity Tanija et al. (1981) derive a regression relation similar to the retention curve, as follows:

$$\log K(h) = a_0 + a_1 \log h + a_2 (\log h)^2 \quad (2.28)$$

Methods for measuring the hydraulic conductivity

The unsaturated hydraulic conductivity is measured either in laboratory on undisturbed samples of soil, or directly in field.

a) Laboratory measurements

Laboratory measurements are carried out either for steady or non-steady flow. The value of the coefficient of unsaturated hydraulic conductivity is determined on the basis of the amount of water which has flowed out during a pressure rise in the apparatus (Fig. 2.7a) the outflow method, or on the basis of water distribution during horizontal infiltration.

b) Field measurements

Field measurements are based on field measurements of pressure head, infiltration rate and water content. The methods for measuring unsaturated hydraulic conductivity are described in detail by Kutřlek (1978), Gardner (1956), Kirkham and Powers (1972), Bruce and Klute (1956), Bouma (1977), and other authors.

Coefficients dependent on soil characteristics, which appear in all the empirical formulas mentioned are best determined by practical measurements in specific situations. Results of practical measurements are also the best basis for the choice of an empirical relation.

2.1.5. Water uptake by the root system

Water uptake by the root system of the vegetation and its time and space distribution over the vertical soil profile depends on the type of vegetation, climatic conditions, the season of the year, soil characteristics and soil water content. Various models describing this process have been given in literature; these models describe this biological process in a rather schematic way. For calculating water uptake by plant roots Feddes et al. (1978) assume linear dependence on the soil water potential in the root zone, accounting for water availability to vegetation defined by hydrolimits:

$$A(h) = A_{\max} (h-h_3)/(h_2-h_3) = \alpha(h) A_{\max} \quad (2.29)$$

where

$$A_{\max} = (E_{\text{plant}}^* / L_k^{\text{EFF}}) \quad (2.30)$$

The value E_{plant}^* is the maximum possible transpiration rate. Figure 2.10 illustrates the relationship given by equation (2.29) Hoogland et al. (1981) modify this model of water uptake by plant roots and consider the value A_{max} varying with depth:

$$A_{\text{max}} = a - b z \quad (2.31)$$

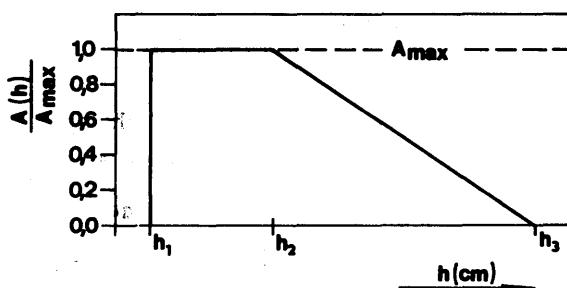


Fig.2.10. Water uptake by plant roots vs soil water potential (after Feddes et al. 1979)

The advantage of using equation (2.29) for water uptake calculation consists in relatively simple input data. Here the root system is characterized by the value L_k^{EFF} only.

The model of Selim, Iskandar (1980) takes into account the vertical distribution of the root system of plants and vertical soil conductivity $K(z)$:

$$A(z,t) = E^* R(z) K(z) / \int_0^z R(z) K(z) dz \quad (2.32)$$

The expression $R(z)$ represents root length (density) as a function of depth z and time t .

The expression describing the distribution of the root $R(z)$ system in equation (2.32) is as follows:

$$R(z) = A \exp (-Bz) \quad (2.33)$$

Saxton et al. (1974) show a distribution of water uptake from various depths of the soil profile dependent on time for corn and grass.

2.1.6. Calculation of the water flow

The partial differential equation describing water flow in the unsaturated zone (2.15) in its analytical form can be solved only for very simplified initial and boundary conditions and for a homogeneous porous medium, i.e. for conditions that are not realistic.

At present numerical mathematical methods are most frequently applied for water flow calculation, especially the finite difference method and the finite element method.

Selim (1980), Tillotson et al. (1980), Tanija et al (1981) and other authors apply the finite difference method in their model solutions. Van Genuchten (1978), Komada (1978) and others have published models of water flow in the unsaturated zone, based on the finite element method.

Milly and Eagleson (1980) have published a model incorporating simultaneous water and heat flow in the unsaturated zone.

The use of numerical methods for the solution of the flow equation together with appropriate initial and boundary conditions makes it possible to model various regimes of underground water flow, following precipitation or irrigation.

At issue is the modelling of saturated and unsaturated infiltration, redistribution and evapotranspiration.

2.1.7. Movement of solute in the unsaturated zone

The nonsteady one-dimensional (vertical) transport of a solute reacting with the soil complex and affected by geochemical (biological, microbial, chemical etc.) reactions can be described by the fundamental equation:

$$\begin{aligned} \partial (\theta C) / \partial t + \partial (\rho S_1) / \partial t = (\partial / \partial z) [D(\theta v) (\partial C / \partial z)] \\ - \partial vC / \partial z \pm Q_1 \end{aligned} \quad (2.34)$$

Coefficient of hydrodynamic dispersion

The coefficient of hydrodynamic dispersion is the sum of the molecular diffusion and mechanical dispersion coefficients. Van Genuchten (1978) gives the following expression for the coefficient of hydrodynamic dispersion:

$$D = D_d \tau + \alpha |v| \quad (2.35)$$

Pickens et al (1979) give the expression

$$D = D_d + \alpha |v| \quad (2.36)$$

where

$$D_d = D_o a \exp (b \theta) \quad (2.37)$$

For the practical determination of the value of the hydrodynamic dispersion coefficient it is best to carry out field tracing tests, or laboratory measurements on undisturbed soil samples.

Adsorption in the soil complex

There are a number of different models for the calculation of solute adsorption in the soil complex (clay, humus, organic matter) presented in literature, these are summarized by e.g. Davidson et al. (1980), van Genuchten (1981). For practical purposes the linear balanced adsorption model (linear adsorption isotherm) is most frequently used Selim (1980), Tillotson et al. (1980), Wagenet (1981), and others.

The quantity of the adsorbed substance S_i is directly proportional to its concentration in the solution:

$$S_i = K_d C_i \quad (2.38)$$

This relation assist the numerical solution of the fundamental transport equation.

Change of solute concentration due to geochemical reactions

In equation (2.34) the symbol Q_i represents a change in concentration caused by various geochemical reactions (chemical, biochemical, microbial, etc.). These processes are of a complex nature, depending often on temperature, pH, the presence of other chemical substances, biological (microbiological) activity in the soil etc.

For their mathematical expression, the kinetics of reactions is most frequently used:

$$\text{reaction of the zero order: } - \frac{dC}{dt} = k_0 \quad (2.39)$$

$$\text{reaction of the 1st order: } - \frac{dC}{dt} = k_1 C \quad (2.40)$$

$$\text{the Michaelis-Menten reaction: } - \frac{dC}{dt} = k_m \frac{C}{k_s + C} \quad (2.41)$$

The kinetic constants k can depend on temperature, soil water content etc.

Van Veen (1980), Tillotson et al. (1980) and other authors treat these problems in more detail.

2.1.8. Calculation of solute movement

The equation of solute movement in the unsaturated zone (2.34) can not be solved in the general analytical form, except for certain simple conditions, e.g. for a homogeneous, porous, medium and for steady-state soil water flow. For practical calculations this simplification is often a too rough an approximation (especially the steady-state flow). Numerical methods are most frequently used here.

Analytical solution

The analytical solution of the transport equation for various initial and boundary conditions is discussed in detail by e.g. van Genuchten (1981). Transport of substance, adsorbed to the soil complex involving a loss of concentration described by the reactive kinetic equation of the first order and an increment (source term) of the 0'th (zero) order, can be described by equation.

$$D \left(\frac{\partial^2 C}{\partial x^2} \right) - v_s \left(\frac{\partial C}{\partial x} \right) - R \left(\frac{\partial C}{\partial t} \right) = \mu C - \gamma \quad (2.42)$$

where μ is a decay constant, γ a source term and R the retardation factor (par. 2.2.9.).

For initial and boundary conditions

$$C(x, 0) = C_1 \quad (2.43)$$

$$C(0, t) = \begin{cases} C_0 & \text{for } 0 < t \leq t_0 \\ 0 & \text{for } t > t_0 \end{cases} \quad (2.44)$$

$$\frac{\partial C}{\partial x}(\infty, t) = 0 \quad (2.45)$$

The solution of the equation has the form of

$$C(x, t) = \begin{cases} (C_0 - \gamma / \mu) H(x, t) + M(x, t) & \text{for } 0 < t \leq t_0 \\ (C_0 - \gamma / \mu) H(x, t) + M(x, t) - C_0 H(x, t - t_0) & \text{for } t > t_0 \end{cases} \quad (2.46)$$

where

$$H(x,t) = \frac{1}{2} \exp \left[(v_s - u)x/2D \right] \operatorname{erfc} \left[(Rx-ut)/2(DRt)^{\frac{1}{2}} \right] + \\ + \frac{1}{2} \exp \left[(v_s + u)x/2D \right] \operatorname{erfc} \left[(Rx+ut)/2(DRt)^{\frac{1}{2}} \right] \quad (2.47)$$

$$M(x,t) = \left(\gamma / \mu - C_1 \right) \exp (-\mu t/R) \left\{ \frac{1}{2} \operatorname{erfc} \left[(Rx-v_s t)/2(DRt)^{\frac{1}{2}} \right] + \right. \\ \left. + \frac{1}{2} \exp (v_s x/D) \operatorname{erfc} \left[(Rx+v_s t)/2(DRt)^{\frac{1}{2}} \right] \right\} + \\ + \left(\gamma / \mu \right) + (C_1 - \gamma / \mu) \exp (-\mu t/R) \quad (2.48)$$

$$u = v_s \left(1 + 4 \mu D/v_s^2 \right)^{\frac{1}{2}} \quad (2.49)$$

Numerical solution

More suitable for the calculation of the movement of chemicals in the unsaturated zone are numerical methods, i.e. mathematical simulation models. These models solve the flow equation simultaneously with the solute transport equation. Of the numerical methods the most frequently applied are the finite difference and finite element methods.

A brief discussion of these methods as well as their merits and demerits are listed in Chapter 2.2.

The following authors describe models based on the finite element method: Kovařík et al. (1982), Mehran et al. (1982), Yeh and Ward (1980), Duguid and Reeves (1976), van Genuchten (1978).

Models based on the finite differences have been published, for example, by Selim and Iskandar (1980), Wagenet (1981) and others.

Application of mathematical simulation models of solute movement in the unsaturated zone which account for all transformation processes that affect agrochemical concentrations, enables the vertical distribution of the solute at an arbitrary moment following application of

Nitrogen contained in fertilizers is applied to the soil surface in the form of NH_4^+ and NO_3^- . Water (precipitation, irrigation) dissolves fertilizers, part of which is drained from the surface together with the surface runoff of water and the greater part infiltrates into soil. Nitrogen is removed from the soil by plant roots. Various soil micro- and macroorganisms cause a number of complex biochemical reactions, in the course of which various transformation processes occur. Ammonia NH_4^+ is nitrified to nitrate NO_3^- , and denitrification processes cause decomposition to gaseous components N_2O and N_2 . These gasses leave the soil partly unused and unchanged and partly as ammonia. Some nitrogen is incorporated into the soil organic matter which is again transformed by mineralization to inorganic matter. Ammonia is also adsorbed by the soil complex. The remaining unused nitrogen, mainly in its nitrate form passes into the groundwater.

2.2. MOVEMENT OF AGROCHEMICALS IN THE SATURATED ZONE

Solute movement in the saturated zone occurs as described in the previous section. The modes of transport are convection and hydrodynamical dispersion. In some cases reaction of solute in water or with rock environment may occur.

2.2.1. Water flow in the saturated zone

When calculating water flow in the saturated zone, a continuous, incompressible, inhomogeneous and anisotropic medium is generally assumed.

Under these assumptions, water flow can be described by equations, similar to those which are mentioned in the previous chapter for water flow in the unsaturated zone, with the difference that now two- or three-dimensional flow should be considered.

For calculating the filtration velocity of flow for an anisotropic, inhomogeneous porous medium the following expressions hold:

Darcy's law

$$v_x = -K_{xx} \left(\frac{\partial h}{\partial x} \right) - K_{xy} \left(\frac{\partial h}{\partial y} \right) - K_{xz} \left(\frac{\partial h}{\partial z} \right) \quad (2.50)$$

$$v_y = -K_{yy} \left(\frac{\partial h}{\partial y} \right) - K_{yx} \left(\frac{\partial h}{\partial x} \right) - K_{yz} \left(\frac{\partial h}{\partial z} \right)$$

$$v_z = -K_{zz} \left(\frac{\partial h}{\partial z} \right) - K_{zx} \left(\frac{\partial h}{\partial x} \right) - K_{zy} \left(\frac{\partial h}{\partial y} \right)$$

Equations (2.50) can be rewritten as a tensor expression

$$v_i = -K_{ij} \left(\frac{\partial h}{\partial x_j} \right) \quad (2.51)$$

where K_{ij} is the tensor of hydraulic conductivity coefficients

$$K_{ij} = \begin{bmatrix} K_{xx} & K_{xy} & K_{xz} \\ K_{yx} & K_{yy} & K_{yz} \\ K_{zx} & K_{zy} & K_{zz} \end{bmatrix} \quad (2.52)$$

and x_i are coordinates.

Placing the coordinate system in the principal direction of the anisotropic medium, the transverse components of the tensor are zero:

$$K_{ij} = 0 \text{ for all } i \neq j$$

$$[K_{ij}] = \begin{bmatrix} K_{xx} & 0 & 0 \\ 0 & K_{yy} & 0 \\ 0 & 0 & K_{zz} \end{bmatrix} \quad (2.53)$$

Equations (2.50) will have a form of

$$v_x = -K_{xx} \left(\partial h / \partial x \right), \quad v_y = -K_{yy} \left(\partial h / \partial y \right),$$

$$v_z = -K_{zz} \left(\partial h / \partial z \right) \quad (2.54)$$

Models accounting for nonlinear relation between velocity and hydraulic gradient are exceptional, and in hydrogeology are seldom encountered.

Equation of continuity

$$S_o \left(\frac{\partial h}{\partial t} \right) = - \frac{\partial v_x}{\partial x} - \frac{\partial v_y}{\partial y} - \frac{\partial v_z}{\partial z} \quad (2.55)$$

Substituting equation (2.55) into (2.51) we obtain the fundamental equation for the unsteady flow:

$$S_o \left(\frac{\partial h}{\partial t} \right) = \left(\frac{\partial}{\partial x_i} \right) \left[K_{ij} \left(\frac{\partial h}{\partial x_j} \right) \right] \quad (2.56)$$

Similarly, substituting equation (2.55) into (2.54) we obtain expression:

$$S_o \left(\frac{\partial h}{\partial t} \right) = \left(\frac{\partial}{\partial x} \right) \left[K_{xx} \left(\frac{\partial h}{\partial x} \right) \right] + \left(\frac{\partial}{\partial y} \right) \left[K_{yy} \left(\frac{\partial h}{\partial y} \right) \right] + \left(\frac{\partial}{\partial z} \right) \left[K_{zz} \left(\frac{\partial h}{\partial z} \right) \right] \quad (2.57)$$

2.2.2. Types of aquifers

According to geological conditions, there are two basic types of aquifers (Fig. 2.12.):

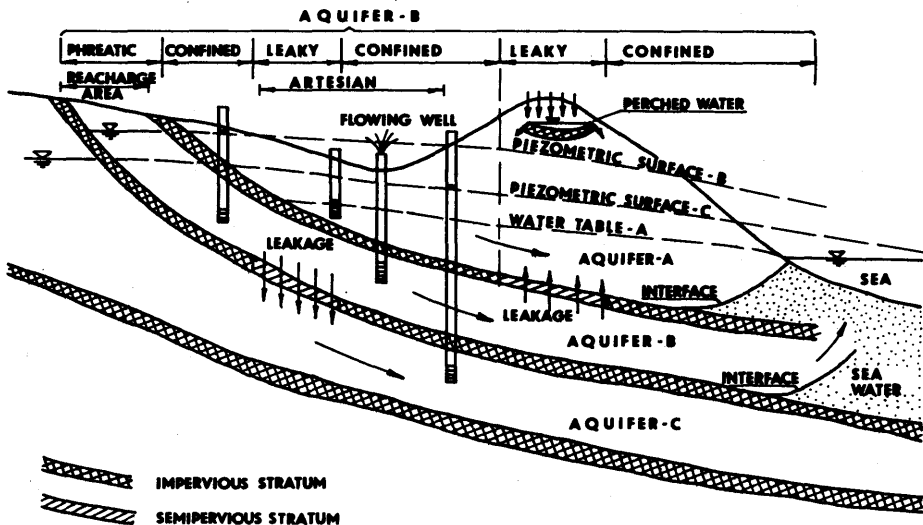


Fig.2.12. Types of aquifers (after Bear, 1979)

a) Phreatic aquifer

The water table of this type of aquifer is at atmospheric pressure and its depth under the earth surface varies, usually dependent on morphological conditions. Phreatic aquifers are usually recharged from precipitation or by leakage from an underlying or overlying aquifer (leaky phreatic aquifer). Drainage areas are determined by morphological conditions and as a rule are not too conspicuous. Groundwater flow is laminar.

b) Confined aquifer (Artensian aquifer)

The aquifer is confined between two relatively impermeable layers, and groundwater is subjected to hydrostatic pressure greater than the atmospheric pressure. This type of aquifers is recharged from precipitation at the outcrop, and/or by leakage from underlying or overlying aquifers (leaky confined aquifer). Areas of drainage are determined by geological and hydrogeological conditions. Groundwater flow is laminar.

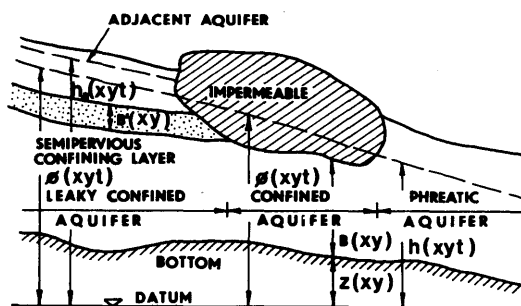


Fig.2.13. Groundwater diagram in respect to transmissivity calculations (after Wilson et al. 1979).

2.2.3. Flow in phreatic aquifer

Integrating equation (2.57) over the saturated thickness b we obtain the fundamental equation of two-dimensional flow for an inhomogeneous and anisotropic medium (Fig. 2.13.):

$$S_y \left(\frac{\partial h}{\partial t} \right) = \left(\frac{\partial}{\partial x} \right) \left[K_{xx} b \left(\frac{\partial h}{\partial x} \right) \right] + \\ + \left(\frac{\partial}{\partial y} \right) \left[K_{yy} b \left(\frac{\partial h}{\partial y} \right) \right] \pm Q_1 \quad (2.58)$$

2.2.4. Flow in confined aquifer

Consider the case of an inhomogeneous and anisotropic aquifer shown in figure 2.13. In calculations of flow in a confined aquifer, transmissivity coefficients are generally used to describe filtration parameters:

$$T_{ij} = K_{ij} B \quad (2.59)$$

Integrating equation (2.57) over the aquifer thickness and adding the source/sink and leakage terms the following two-dimensional flow expression is obtained:

$$S \left(\frac{\partial \phi}{\partial t} \right) = \left(\frac{\partial}{\partial x} \right) \left[T_{xx} \left(\frac{\partial \phi}{\partial x} \right) \right] + \\ + \left(\frac{\partial}{\partial y} \right) \left[T_{yy} \left(\frac{\partial \phi}{\partial y} \right) \right] + \left(\frac{K'}{B} \right) (h_a - \phi) \pm Q_1 \quad (2.60)$$

2.2.5. Radial flow

Equation (2.60) can be transformed into the polar coordinate system, assuming axially symmetrical radial flow in a homogeneous and isotropic porous medium and neglecting recharge (discharge into) from the control area:

$$(S_y/T) \left(\partial h / \partial t \right) = \left(\partial^2 h / \partial r^2 \right) + (1/r) \left(\partial h / \partial r \right) \quad (2.61)$$

This form of the equation is the most frequently used for evaluation of hydrodynamic tests (pumping tests) under the steady-state as well as unsteady flow conditions. For more detail see e.g. Bear (1979), Kruseman and De Ridder (1970) and other authors.

2.2.6. Coefficients of specific storage

The coefficient of specific storage is the degree to which an aquifer is capable of releasing or receiving a certain volume of water by its unit volume when a unit water head drop (or increase) occurs. In the case of phreatic aquifer the coefficient of specific storage is practically equal to the effective porosity divided by the thickness of the aquifer. In the case of confined aquifer the coefficient of storage depends on the porous medium deformation.

Coefficient of storage for a phreatic aquifer

The coefficient of storage for a phreatic aquifer (in literature often denoted as specific yield) can be expressed by the relation

$$S_y = n - S_r \quad (2.62)$$

The Symbol S_r denotes the coefficient of specific retention (the amount of water retained in the pores of a rock by capillary forces), and n denotes the overall porosity.

Values S_y , n and S_r are schematically illustrated in figure 2.14.

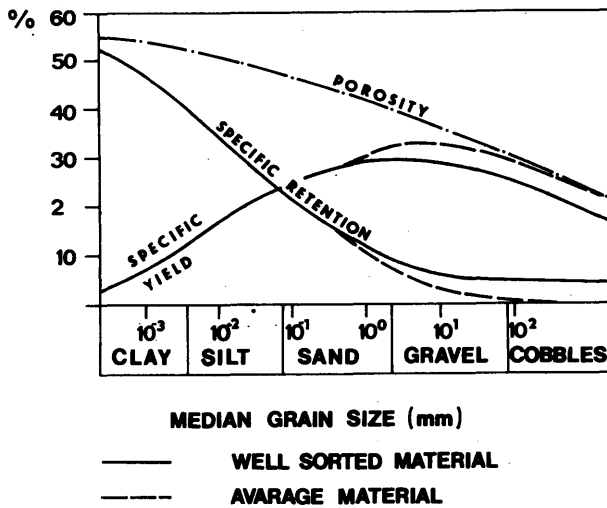


Fig.2.14. Relationship between specific yield, specific retention, porosity and grain size (after Davis and De Wiest, 1966).

Coefficient of storage for a confined aquifer

In calculations of water flow in a confined aquifer, the filtration parameters are usually described by transmissivity coefficients (see equation (2.59), where $T = K.B$). For the coefficient of storage the analogous expression $S = S_o.B$ is used.

The value of the coefficient of storage S for the confined aquifer is distinctly lower than that for the phreatic aquifer and its magnitude is of the order of 10^{-4} to 10^{-7} .

Coefficients of storage can be determined by means of one of the hydrodynamic tests directly in the field.

2.2.7. Coefficients of hydraulic conductivity

For specific cases the coefficients of hydraulic conductivity can be determined by a field hydrodynamic test (pumping, injection, withdrawal etc.), see e.g. Kruseman, de Ridder (1976). Laboratory measurements on undisturbed soil samples give less precise coefficients of hydraulic conductivity. Hydraulic conductivity coefficient values calculated from various empirical formulas (see e.g. Bear 1979) incorporating the influence of geometrical properties of the infiltration environment are of little practical use. Hydraulic conductivity coefficients for various soil types are given in table 2.1.

Table 2.1. Typical values of hydraulic conductivity and permeability (after Bear, Zaslavsky and Irmay, 1968)

$-\log_{10} K \text{ (cm.s}^{-1}\text{)}$	-1	0	1	2	3	4	5	6	7	8	9	10	11	
Permeability	Pervious			Semipervious				Impervious						
Aquifer	Good				Poor				None					
Soils	Clean gravel	Clean sand or sand and gravel			Very fine sand, silt, loess, loam, solonetz									
				Peat		Stratified clay			Unweathered clay					
Rock				Oil rock				Sandstone		Limestone dolomite		Breccia, granite		
$-\log_{10} k \text{ (cm}^2\text{)}$	3	4	5	6	7	8	9	10	11	12	13	14	15	16

When investigating the flow of various liquids in porous media, the coefficient of permeability k is introduced in order to express the effect of their physical properties (specific mass and viscosity):

$$k = K (\nu/g) \quad (2.63)$$

For water with a temperature of 20°C the following relation between coefficients of conductivity and of permeability holds:

$$1 K (\text{cm.s}^{-1}) = 1.02 \times 10^{-5} k (\text{cm}^2) \quad (2.64)$$

2.2.8. Coefficients of transmissivity

The transmissivity coefficient is the product of the hydraulic conductivity coefficient and the depth of the aquifer. In the case of a confined aquifer the following expressions for transmissivity coefficients are valid:

$$T_{xx}(x,y,t) = K_{xx}(x,y) B(x,y),$$

$$T_{yy}(x,y,t) = K_{yy}(x,y) B(x,y) \quad (2.65)$$

In the case of a phreatic aquifer the transmissivity coefficients are a function of time-varying water table level:

$$T_{xx}(x,y,t) = K_{xx}(x,y) [h(x,y,t) - z(x,y)] = K_{xx}(x,y) b(x,y,t) \quad (2.66)$$

$$T_{yy}(x,y,t) = K_{yy}(x,y) [h(x,y,t) - z(x,y)] = K_{yy}(x,y) b(x,y,t) \quad (2.67)$$

Transmissivity coefficient values are obtained by similar methods as hydraulic conductivity coefficients.

Field hydrodynamic tests are most suitable for this purpose.

2.2.9. Movement of solutes in the saturated zone

The non-stationary movement of solute in groundwater, in anisotropic inhomogeneous porous medium can be described by a general equation:

$$\begin{aligned} \partial C / \partial t = & \left(\partial / \partial x_i \right) \left[D_{ij} \left(\partial C / \partial x_j \right) \right] - \left(\partial (v_{si} C) / \partial x_i \right) \\ & - \left(\rho / n_o \right) \left(\partial S_i / \partial t \right) \pm q_i \end{aligned} \quad (2.68)$$

The velocity of water flow can be calculated:

$$v_{si} = (K_{ij} / n_o) \left(\partial h / \partial x_i \right) \quad (2.69)$$

A two-dimensional transport model is most frequently used in the practical investigation of the spread of contamination. Equation (2.68) can be expressed in the form of

$$\begin{aligned} \partial C / \partial t = & \left(\partial / \partial x \right) \left[D_{xx} \left(\partial C / \partial x \right) \right] + \\ & + \left(\partial / \partial x \right) \left[D_{xy} \left(\partial C / \partial x \right) \right] + \left(\partial / \partial y \right) \left[D_{yx} \left(\partial C / \partial y \right) \right] + \\ & + \left(\partial / \partial y \right) \left[D_{yy} \left(\partial C / \partial y \right) \right] - \left(\partial / \partial x \right) \left(C v_{sx} \right) - \\ & - \left(\partial / \partial y \right) \left(C v_{sy} \right) - \left(\rho / n_o \right) \left(\partial S_i / \partial t \right) \pm q_i \end{aligned} \quad (2.70)$$

Assuming one-dimensional flow along the x-axis, the equation (2.68) can be rewritten in the form:

$$\begin{aligned} \partial C / \partial t = & \left(\partial / \partial x \right) \left(D_L \left(\partial C / \partial x \right) \right) + \\ & + \left(\partial / \partial y \right) \left(D_T \left(\partial C / \partial y \right) \right) - v_{sx} \left(\partial C / \partial x \right) - \left(\rho / n_o \right) \left(\partial S_1 / \partial t \right) \pm q_1 \end{aligned} \quad (2.71)$$

For an isotropic, homogeneous, porous medium, for a substance inert to the rock medium, without gains or losses of the transported substance, and assuming one-dimensional groundwater flow in the direction of the x-axis, the transport equation has the form of

$$\begin{aligned} \partial C / \partial t = & D_L \left(\partial^2 C / \partial x^2 \right) + D_T \left(\partial^2 C / \partial y^2 \right) - \\ & - v_{sx} \left(\partial C / \partial x \right) \end{aligned} \quad (2.72)$$

Bearing in mind the dependence of solute adsorption on its concentration (following the Freundlich linear isotherm), then

$$S_1 = K_d C \quad (2.73)$$

The adsorption rate can be expressed as a time-derivative of equation (2.73)

$$\partial S_1 / \partial t = K_d \left(\partial C / \partial t \right) \quad (2.74)$$

Equation (2.71) can then be expressed in the form of

$$\begin{aligned} \left(1 + \left(\rho / n_o \right) K_d \right) \left(\partial C / \partial t \right) = & \left(\partial / \partial x \right) \left(D_L \left(\partial C / \partial x \right) \right) + \\ & + \left(\partial / \partial y \right) \left(D_T \left(\partial C / \partial y \right) \right) - v_{sx} \left(\partial C / \partial x \right) \pm q_1 \end{aligned} \quad (2.75)$$

The expression $(1 + (\rho/n_o) K_d)$ is given in literature as the retardation factor R (Pickens et al. 1979).

Equation (2.70) and (2.72) can be modified in a similar manner.

2.2.10. Coefficient of hydrodynamic dispersion

The coefficient of hydrodynamic dispersion D_{ij} is a tensor of the second order.

With the help of field tracing tests the longitudinal coefficient of hydrodynamic dispersion D_L (in the flow direction), and the transverse coefficient D_T (perpendicular to the flow direction), can be determined. Individual components of tensor D_{ij} can be calculated for two-dimensional flow and transport:

$$D_{xx} = D_L ((v_x)^2 / |v|^2) + D_T ((v_y)^2 / |v|^2)$$

$$D_{yy} = D_T ((v_x)^2 / |v|^2) + D_L ((v_y)^2 / |v|^2)$$

$$D_{xy} = D_{yx} = (D_L - D_T) (v_x v_y / |v|^2) \quad (2.76)$$

The coefficient of hydrodynamic dispersion incorporates the influence of molecular diffusion and mechanical dispersion

$$D_H = D + D_d \quad (2.77)$$

and in general depends on the following parameters (Fried, 1975):

- the viscosity of both liquids
- difference in the density of both liquids
- water flow rate
- characteristics of the porous medium (granulometry, shape and surface of grains, porosity, hydraulic conductivity coefficient etc.)

These relations can be expressed in the following general form:

$$D_H = f(\mu_1, \mu_2, \Delta\rho, D_d, v, d, g) \quad (2.78)$$

Experimental measurements in field or on intact samples of rock in laboratory will not provide an expression of the dependence of the hydrodynamic dispersion coefficient on all listed parameters. The most frequently used are the dependence of the hydrodynamic dispersion coefficient on the groundwater flow velocity and on the properties of rock, which are represented by a general coefficient (mechanical dispersivity) and by molecular diffusion (diffusivity and tortuosity). Yeh and Ward (1981) consider the relation

$$D_L = \alpha_L |v| + D_d \tau, \quad D_T = \alpha_T |v| + D_d \tau \quad (2.79)$$

Bear (1979) and some other authors consider tortuosity as a tensor of the second order.

Klotz and Moser (1980) use a relation in the form of

$$D_L = \alpha_L |v|^n \quad (2.80)$$

$$D_T = \alpha_T |v|^m \quad (2.81)$$

Konikov, Bredehoeft (1978) and other authors consider the exponent in equations (2.80) and (2.83) to be equal to 1 and use linear relations

$$D_L = \alpha_L |v| \quad (2.82)$$

$$D_T = \alpha_T |v| \quad (2.83)$$

For practical purposes, the most suitable are expressions described by equation (2.82) and (2.83), because in field measurements the overall coefficient of hydrodynamic dispersion is determined, and that includes effects of mechanical dispersion as well as molecular diffusion.

Determination of the coefficient of hydrodynamic dispersion (dispersivity)

The most accurate method to determine the coefficient of hydrodynamic dispersion is a field tracing test.

The tracer (NaCl solution, colors, radioisotopes) is dosed in a defined manner into the injection well (disturbance signal) and in other observation wells (or by means of surface geophysical detection) the time-space distribution of the tracer in the aquifer is monitored.

Tracing tests results (residence time distribution function) are generally processed assuming that the tracer is moving in a homogeneous and isotropic porous medium.

Fried (1975) classifies field methods for determination of dispersion coefficients according to the scale used

- a) local scale - between 2 to 4 meters
- b) global scale I - between 2 to 20 meters
- c) global scale II - between 20 to 200 meters
- d) regional scale - more than 100 meters

Individual methods correspond to the experimental techniques of field measurements:

- a) Local scale - the single well pulse technique - the tracer is dosed into the well via pure water inflow (injection test). The tracer is forced into the aquifer and during subsequent pumping of water from the well, the tracer returns to the well. Concentration of the tracing substance is measured during the whole test.

b) Global scale I - the multiple wells method - the tracer is either dosed in pulses or continually into the injection well and the response to the input signal is measured in a series of observation wells situated in the direction of flow.

c) Global scale II - the single well method - the tracer is dosed into the injection well and its spreading is detected with the use of the surface geophysical method.

d) Regional scale - use of environment tracers - i.e. the existing pollution sources, natural isotopes etc. Verification of dispersion parameters calculated in this way usually requires application of model techniques. The problems of laboratory and field determination of the hydrodynamic dispersion coefficients are treated in fuller detail by Fried (1975), Klotz and Moser (1980), Beneš et al. (1982) and other authors.

Values of longitudinal dispersivity published by different authors lie in the range of 0.1 to 15.0 meters.

Dispersivity values determined by some authors using different methods of field tests are listed in table 2.2.

Table 2.2. Coefficients of longitudinal dispersivity (after Jackson et al. 1980)

REFERENCE	TYPE OF TEST	DISTANCE BETWEEN WELLS (m)	SLOTTED LENGTH OF WELLS (m)	LONGITUDINAL DISPERSIVITY (m)
Theis (1963)	Natural	3500	n.r.	6
Percious (1969)	Single-well injection-withdrawal	n.a.	30,5	0,08 to 0,25
Wilson (1971) (in Robson 1974)	Two-well recirculating	79,2	14,6	15,2
Wilson (1971)	Single-well inject.-withdrawal	n.a.	15,2	0,25 to 0,33
Fried et al. (1972)	Single-well pulse individual layers	n.a.	0,25 layers	0,1 to 0,6
Kreft et al. (1974)	Two-well pulse	5 of 6	n.r.	D/v = 0,18
Robson (1974)	Two-well recirculating	6,4	27,4	15,2
Fried (1975)	Natural gradient radial injection	< 12 n.r.	n.r. n.r.	4,25 11,0
Grisak (1977) (personal communication)	Single-well injection-withdrawal	n.r.	1,8	0,29
Peaudecerf and Sauty (1978)	Uniform gradient	12		1 to 2,7
Sauty (1987)	Two-well pulse	9 6	n.r. n.r.	6,9 0,3
Sudicky and Cherry (1979)	Natural gradient	0,8 to 14	point sampling	0,1 to 0,22
Sauty et al. (1979)	Single-well injection-withdrawal - central well - observation wells	n.a. < 13	n.r. n.r.	1 0,8 x radius
Lee et al. (1980)	Natural gradient	< 6	point sampling	0,012

Note: n.r. = not reported
n.a. = not applicable

2.2.11. Mathematical solution of the flow and transport equations

Analytical solution

Analytical solution of the flow equation is possible for a homogeneous and isotropic medium and steady-state flow (see e.g. Thiem, Dupuit, equation for steady-state flow into well), or the approximate analytical-graphic Theis' solution is feasible, also its simplified Jacob's version, etc. Analytical solution of the flow equation is most frequently used in connection with description of methods for pumping test evaluation. This problem area is treated in greater detail by Bear (1979), Kruseman and De Ridder (1976), Verigin (1962), Skabalonović (1960), Walton (1962) and other authors.

Analytical solution of the transport equation is similarly limited and is feasible only for a homogeneous and isotropic medium, steady-state groundwater flow and simple initial and boundary conditions. The analytical solution of the transport equation is often used for evaluation of field measurements - e.g. tracing tests for determining the hydrodynamic dispersion coefficient.

For the most frequently used tracing test, pulse injection of the tracing substance into the well (disturbance signal in the form of Dirac's function), Klotz et al. (1980) give the following solution of equation (2.72):

Boundary conditions:

$$C(x = 0, y, t) = (A/n_o h v_g) \delta(y) \delta(t)$$

$$\lim_{x \rightarrow \infty} C(x, y, t) = 0$$

$$x \rightarrow \infty$$

$$\lim_{y \rightarrow \infty} C(x, y, t) = 0$$

$$y \rightarrow \infty$$

A is the added tracer amount

initial conditions:

$$C(x, y, t = 0) = 0 \quad \text{for } x > 0, y \neq 0$$

$$C(x, y, t) = \frac{A}{4 n_o \pi h t (D_L D_T)^{\frac{1}{2}}} \exp - \left[\frac{(x - v_s t)^2}{4 D_L t} + \frac{y^2}{4 D_T t} \right] \quad (2.85)$$

Values of the hydrodynamic dispersion coefficients can be calculated from simple expressions

$$D_L = (\sigma_L^2 / 2 t) \quad (2.86)$$

$$D_T = (\sigma_T^2 / 2 t) \quad (2.87)$$

where σ is the standard deviation of concentration-time of the solute distribution.

The analytical solution of the transport equation for various types of boundary and initial conditions is described in detail by Bear (1979), Rushton (1977), van Genuchten (1980) and other authors.

Numerical solution

For practical calculations of contaminant movement in groundwater numerical mathematical methods (mathematical simulation models) are applied, which make the solution of the flow and transport equations possible for an inhomogeneous and anisotropic porous medium, for unsteady flow and for various types of initial and boundary conditions.

Numerical solution normally involves approximating continuous partial differential equations with a set of discrete equations in time and space. Thus the area and time period of interest are divided in some fashion, resulting in an equation or a set of equations for each area

and time step. These discrete equations are combined to form a system of algebraic equations that must be solved for each time step. Finite difference and finite element methods are the major numerical techniques used in groundwater applications. The important components and steps of model development for the two alternative methods are shown in figure 2.15.

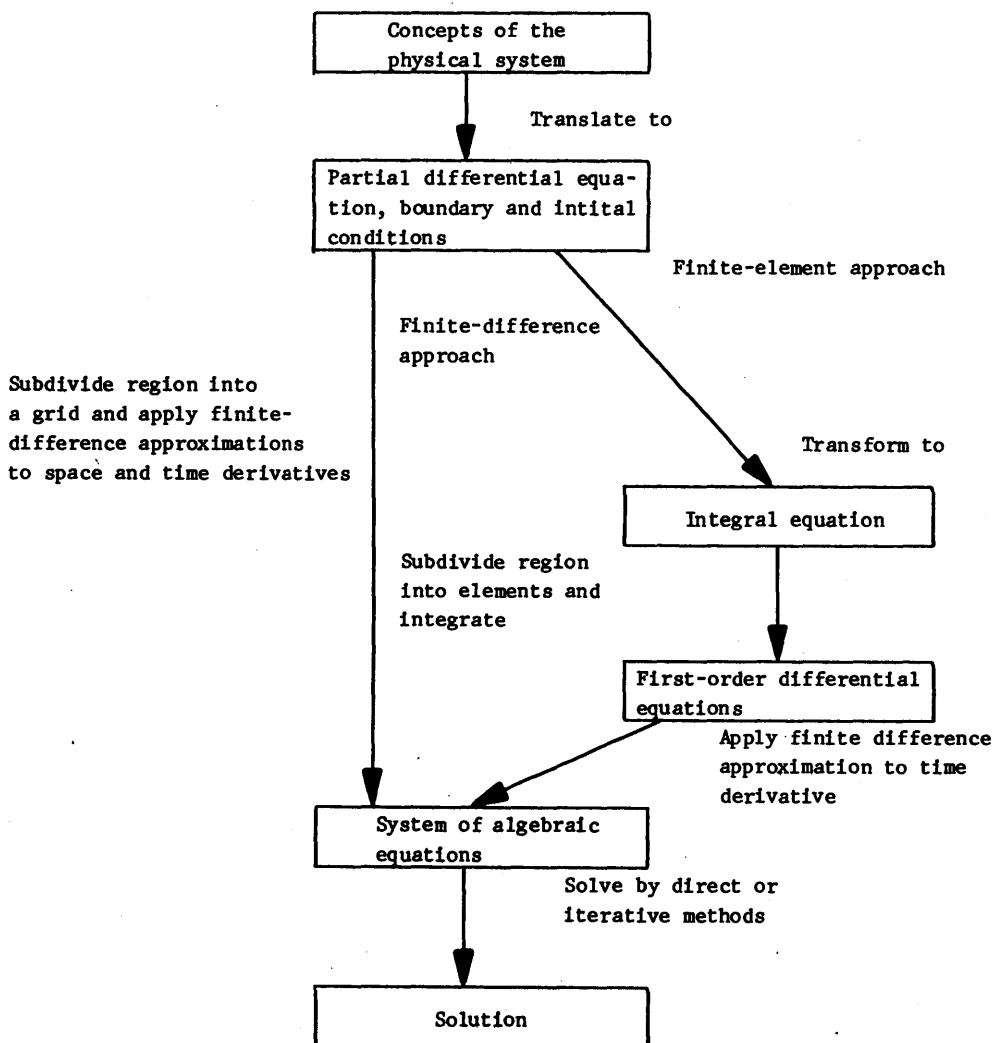


Fig.2.15. Generalized model development by finite-difference and finite-element methods.

A more detailed description of both methods is given by e.g.: finite differences - Scarborough (1966), van Rosenberg (1969), Pinder and Bredehoeft (1969), Trescott and Larson (1976); finite elements - Desai and Abel (1972), Zienkiewicz (1971), Huebner (1975), Brebia (1974) and other authors.

The method of characteristics is another numerical method used in solving the transport equation, and is described by e.g. Garder, Peaceman and Pozzi (1964), Reddel and Sunada (1971), Konikov and Bredehoeft (1978) and others.

The essential merits and demerits of individual methods are presented by Faust and Mercer (1980) and listed in table 2.3.

Table 2.3. Brief summary of important advantages and disadvantages of FDM and FEM (as they are commonly used) (after Faust and Mercer, 1980)

ADVANTAGE	DISADVANTAGES
FINITE-DIFFERENCE METHOD	
Intuitive basis	Low accuracy for some
Easy data input	problems
Efficient matrix techniques.	Regular grids.
FINITE-ELEMENT METHOD	
Flexible geometry.	Mathematical basis is
High accuracy easily included.	advanced.
Evaluates cross-product terms better.	Difficult data input.
	Difficult programming.

Initial and boundary conditions

Both analytical and numerical solution of the water flow and transport equations require specification of boundary conditions.

Types of boundary conditions applicable for solving both equations are listed in table 2.4.

Table 2.4. Groundwater boundary conditions (after Mercer, Faust, 1980)

Type	Description
Specified Value	Values of head, concentration or temperature are specified along the boundary. (In mathematical terms, this is known as the Dirichlet condition).
Specified Flux	<p>Flow rate of water, concentration or temperature is specified along the boundary and equated to the normal derivative. For example, the volumetric flow rate per unit area for water in an isotropic media is given by</p> $q_n = -K \left(\frac{\partial h}{\partial n} \right)$ <p>where the subscript n refers to the direction normal (perpendicular) to the boundary. A no-flow (impermeable) boundary is a special case of this type in which $q_n = 0$. (When the derivative is specified on the boundary, it is called a Neumann condition.)</p>
Value-Dependent Flux	<p>The flow rate is related to both the normal derivatives and the value. For example, the volumetric flow rate per unit area of water is related to the normal derivative of head and head itself by</p> $-K \left(\frac{\partial h}{\partial n} \right) = q_n(h_b)$ <p>where q_n is some function that describes the boundary flow rate given the head at the boundary (h_b).</p>

Initial conditions are boundary conditions specified with respect to time (e.g. groundwater potential or contaminant concentration in time).

Mathematical simulation models make calculations possible forecasting contaminant spread in groundwater, active protection of groundwater from pollution, and/or remedial measures in case of previously contaminated water.

A survey of some mathematical models of water flow and of solute transport in the saturated zone is presented in table 2.5.

Table 2.5. Survey of models of groundwater flow and solute transport
in the saturated and saturated-unsaturated zone

TYPE OF PROBLEM	MODELS	MATHEMATICAL SOLUTION METHOD	REFERENCES
FLUID FLOW			
SATURATED ZONE			
Two-dimensional flow	Aquifer I, II	FDM	Pinder (1968)
Two-dimensional flow	Aquifem	FEM	Wilson et al. (1980)
Two-dimensional flow	FLUMP	FEM	Neuman (1970)
Two-dimensional flow	MICHIGAN	FEM	Wingert (1974)
Two-dimensional flow	FRESURF	FEM	Neuman (1971)
Two-dimensional flow	ISOQUAD 2	FEM	Pinder and Frind (1972)
Two-dimensional flow	SAMIR	FEM	Armisen et al. (1975)
Two-dimensional flow	HOREC	FDM	Luckner and Schestakov (1975)
Two-dimensional flow	SOPH	FDM	Vandenberg (1974)
Three-dimensional flow	INTERA HCTM	FEM	INTERA Environmental Consul. Houston USA (1971)
Three-dimensional flow	DAVIS FE	FEM	Gupta et al. (1975)
Three-dimensional flow	WALES Eng	FEM	France (1974)
Three-dimensional flow	USGS (3 D)	FDM	Trescott (1975)
Three-dimensional flow	HANDFORD VII	FDM	Kipp et al. (1972)
Three-dimensional flow	COOLEY	FEM	Coley (1974)
SATURATED - UNSATURATED ZONE			
Two-dimensional (flow vertical plane)	OAK RIDGE I	FEM	Reeves and Duguid (1975)
Two-dimensional (flow vertical plane)	OAK RIDGE II	FEM	Yeh and Ward (1980)
Two-dimensional (flow vertical plane)	NEUMAN FE	FEM	Neuman (1972)
Three-dimensional flow	COLORADO	FDM	Brutsaert (1973)
Three-dimensional flow	SEGOLFE	FEM	Segol (1976)
Two-dimensional flow	PRINCETON	FEM	van Genuchten and Pinder (1978)

Table 2.5. Continued

TYPE OF PROBLEM	MODELS	MATHEMATICAL SOLUTION METHOD	REFERENCES
CONTAMINANT TRANSPORT			
SATURATED ZONE			
Two-dimensional advection transport of conservative sub- stance-horizontal	HANFORD PCP	PCP	Friedrichs (1976)
Two-dimensional advection transport of conservative sub- stance-horizontal	FLOP	PCP	Van Den Akker (1974)
Two-dimensional advection transport of conservative sub- stance-horizontal	FRONT	MCH	Vandenberg (1974)
Three-dimensional advection and dis- persion transport of conservative substances	INTERA CTM	MCH	INTERAL Environmental consult. Inc. Houston USA (1979)
Three-dimensional advection and dis- persion transport of conservative substances	SEGOL	FEM	Segol (1976)
Two-dimensional advection and dis- persion transport of conservative substances-hori- zontal	USGS MC	FDM + MCH	Konikov Bredehoeft (1974)
Two-dimensional advection and dis- persion transport of conservative substances-hori- zontal	ISOQUAD	FEM	Pinder and Frind (1972)
Two-dimensional advection and dis- persion transport of conservative substances-verti- cal	MC	MC	Llamas (1978)

Table 2.5. Continued

TYPE OF PROBLEM	MODELS	MATHEMATICAL SOLUTION METHOD	REFERENCES	
CONTAMINANT TRANSPORT				
SATURATED ZONE				
Two-dimensional advection and dispersion transport of conservative substances-horizontal	MMT-DPRW	RW	Ahlstrom and Foote	(1976)
Two-dimensional advection and dispersion transport of conservative substances-horizontal	SCHWARTZ	FDM - MCH	Schwartz	(1973)
Two-dimensional advection and dispersion transport of conservative substances-horizontal	REFQS	FEM	Scheaffer	(1974)
Three-dimensional advection and dispersion transport of conservative substances-	FEM	FEM	Kovařík et al.	(1983)
SATURATED-UNSATURATED ZONE				
Two-dimensional advection and dispersion transport of reactive substances-vertical	FET	FEM	Duguid, Reeves	(1975)
Two-dimensional advection and dispersion transport of reactive substances-vertical	FEMWASTE	FEM	Yeh, Ward	(1981)
L E G E N D				
FEM	finite element method			
FDM	finite difference method			
MCH	method of characteristic			
MC	mixing Cell			
PCP	path line method			
RW	random walk method			

List of symbols

TERM	SYMBOL	UNIT
rate of water extraction by plants	A (zt)	s^{-1}
maximum rate of water extraction by plants	A_{max}	s^{-1}
thickness of phreatic aquifer	b	m
thickness of confined aquifer	B	m
concentration of dissolved chemicals	C	$g.m^{-3}$
differential soil water capacity	c (h)	m^{-1}
initial and boundary concentration	C_1, C_o	$g.m^{-3}$
soil water diffusivity	D (θ)	$m.^2.s^{-1}$
unsaturated coef. of hydrodynamical dispersion	D (θv)	$m.^2.s^{-1}$
coefficient of molecular diffusion	D_d	$m.^2.s^{-1}$
coefficient of molecular diffusion in water	D_o	$m.^2.s^{-1}$
average diameter of grain	d	m
coefficient of hydrodynamical dispersion	D_{ij}	$m.^2.s^{-1}$
coefficient of longitudinal hydrodynamic dispersion	D_L	$m.^2.s^{-1}$
coefficient of transverse hydrody- namic dispersion	D_T	$m.^2.s^{-1}$
maximum transpiration	E_{plant}	$m.s^{-1}$
piezometric head of a phreatic aquifer	h	m
total hydraulic potential	H	m
soil water potential	h	m
soil water potential for point of air entrance	h_a	m
limit. soil water potential	h_{lim}	m
coefficient of conductivity	K	$m.s^{-1}$
coefficient of permeability	k	m^2

TERM	SYMBOL	UNIT
rate constant of reaction order 0 (zero)	k_0	s^{-1}
rate constant of reaction order 1	k_1	s^{-1}
Michaelis constant	k_m	s^{-1}
max. rate of reaction	k_s	-
unsaturated hydraulic conductivity	$K(h)$	$m.s^{-1}$
saturated hydraulic conductivity	K_o	$m.s^{-1}$
distribution coefficient	K_d	$m^3.g^{-1}$
hydraulic conductivity (tensor 2nd order)	K_{ij}	$m.s^{-1}$
vertical hydraulic conductivity	K'	$m.s^{-1}$
distance	L	m
max. depth of roots	L_k^{EFF}	m
solid soil bulk	m_z	g
water mass	m_w	g
porosity	n_o	-
source or sink function	Q_i	$g.m^{-3}.s^{-1}; m.s^{-1}$
root distribution function	$R(z)$	-
history factor	R	-
retardation factor	$R = 1 + (\rho / n_o) K_d$	-
Reynolds number	Re	-
radial coordinate	r	m
soil physical properties	R	-
water saturation	S_w	-
exchangeable phase of substances	S_i	-
coefficient of specific retention	S_r	-
coefficient of storage for phreatic aquifer (specific yield)	S_y	-
coefficient of storage for confined aquifer	$S = B . S_o$	-
coefficient of specific storage	S_o	m^{-1}
coefficient of transmissivity	T_{ij}	$m^2.s^{-1}$
time	t	s
mean time	\bar{t}	s

TERM	SYMBOL	UNIT
soil temperature	T	°C
water velocity (filtration)	v	m.s ⁻¹
water flow velocity (effective velocity)	v _s	m.s ⁻¹
soil sample volume	V _s	m ³
water volume	V _w	m ³
volume of pores	V _p	m ³
gravimetric water content	w	-
coordinate	x,y,z	m
dispersivity coefficient	α	m
rate constant order 1	μ	s ⁻¹
rate constant order 0 (zero)	γ	g.m ⁻³ .s ⁻¹
residual water content	θ _r	-
saturated water content	θ _s	-
volumetric water content	θ	-
mercury bulk density	ρ _m	g.m ⁻³
soil bulk density	ρ _s	g.m ⁻³
water bulk density	ρ _w	g.m ⁻³
tortuosity	τ	-
Dirac's δ function for y	δ (y)	-
Dirac's δ function for t	δ (t)	-
kinematic viscosity	ν	m ² .s ⁻¹
dynamic viscosity	μ	Pa.s
piezometric head of a confined aquifer	φ	m

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3. IMPACT OF FERTILIZERS AND PESTICIDES ON GROUND-WATER QUALITY.

V. HOUZIM, J. VÁVRA, J. FUKSA, V. PĚKNÝ, J. VRBA and
J. STIBRAL.

3.1. INTRODUCTION

Agriculture as practiced for centuries in many regions has entirely changed the original natural ecosystem. Its progressive transformation through ploughing, sowing, the use of organic and inorganic fertilizers and pesticides, irrigation and draining, has led to interactions between the vegetation, soil, water and rock systems. Superfluous components introduced by man into the agrosystem store, accumulate, assimilate and transform in soil or often are leached from soil into surface or groundwater. The quality of water then degrades and its suitability and economic value as a water supply is reduced.

Methods of contemporary agriculture have changed from crop rotation to monoculture and from single to mass animal breeding. The application of continuous and increasing doses of inorganic fertilizers and pesticides has led in many regions to conflicts between agriculture and water users. Economic interests in agriculture, one of the most important sectors in a country's economy, have become of considerable significance. The ecological consequences of agricultural activities have been pushed into the background. One reason for this is that the negative impact of agriculture on the ecosystem, especially on groundwater, is usually delayed.

Increases in soil fertility and crop yields have been attained, especially since 1960, by massive applications of inorganic fertilizers. During the past twenty years, but mainly between 1960 and 1970, the use of fertilizers in Europe has doubled, often with serious consequences to groundwater quality. A statistical relationship has

been demonstrated between the amount of nitrogen fertilizers applied and the nitrogen content of groundwater. However, concomitant increases in weed growth, crop diseases and animal pests tended to reduce annual increases in crop yields, according to several sources, between 22 and 35 per cent. Hence a greatly increased use of herbicides, anti-disease sprays, and particularly farm pesticides was called for.

The current annual world production of pesticides is about 10 million tonnes, of which more than 80 per cent are produced in Europe and the U.S.A.. During the past twenty years, the use of pesticides in agriculture has grown fourfold.

Most pesticides have a low solubility in water and their movement is generally limited in soil systems. But occurrences of pesticide residues in groundwater are reported as a consequence of agricultural activity. Pest management and policies should be established in each country with the objective of reducing the environmental side effects of pesticides.

Soil organic matter is of special importance for the transport and transformation of fertilizers and pesticides in the unsaturated zone. Soil organic matter is

1. environment and energy source for soil microorganisms which affect biological sorption of fertilizers and biological degradation of pesticides,
2. a component positively influencing soil hydrophysical properties and the transport of substances dissolved and dispersed in water,
3. a component which affects the soil's sorption ability; the exchange capacity increases with the growing stability of the soil organic matter components, and reaches up to 300 mequiv/100 g for fulvic acids and up to 600 mequiv/100 g for humic acids,
4. a source of nutrients, including nitrogen, as a potential contaminant. The amount of nitrogen bound in the soil organic matter is estimated at tonnes to tens of tonnes per one hectare of arable land, depending on the type and condition of the soil.

3.2. ORGANIC FERTILIZERS

Organic fertilizers in varying amounts have been applied by man to arable land and pasture for centuries. They contain all essential nutrients such as nitrogen, potassium and phosphorus, stimulators such as mucins, auxin and heteroauxin, to restore humus reserves in soil and improve the soil structure and sorption capacity.

Organic fertilizers commonly include faeces or solid ("farmyard") manure, liquid manure, slurry, dung water, green manure, straw and compost.

Soil which has not been supplied with organic fertilizers for some time loses its biological activity, its fertility declines, and its bioenergy potential drops. Thus such fertilizers play a versatile role and restore to the soil plant nutrients and humus essential above all to utilize effectively the steadily growing doses of artificial inorganic fertilizers put into the soil.

Farm manure supplies soil with some important growth stimulators and also a considerable quantity of microbes that support biological activity and are essential for mineralizing nutrients. Organic fertilizers directly affect plant nutrition and the nutrient level in the soil, and indirectly affect physical, chemical and, above all, biological processes occurring in the soil.

Organic fertilizers account for 40 per cent of the humus component created in soil. An increased content of humus increases the soil water holding capacity, the adsorption capability, and the resistance of the soil to acidification.

3.2.1. Types of organic fertilizers

Solid manure is a mixture of solid and semisolid faeces of domestic animals and litter, a product of decomposition processes operating in a dung-hill.

Liquid manure is a product of solid faeces and urine, and sometimes a small amount of litter. The excessive application of liquid (especially pig) manure on slopes directly affects the quality of surface and groundwater.

Slurry is a mixture of solid faeces and urine diluted with water. Dung water is the decomposed urine of domestic animals diluted to varying degrees with water, minus the highly volatile ammonium nitrogen. As well as urea it also contains the uric, benzoic and hippuric acids, and some other substances such as auxins and heteroauxins with stimulative action. Dung water is not suitable for direct use on arable land in hydrogeologically sensitive areas.

Green manuring is the working of plants grown for this special purpose into soil. The most frequently grown plants for green manuring are cruciferous and leguminous plants, various kinds of grass, or their mixtures. The first of the above-mentioned plants are important fixers of atmospheric nitrogen.

Farm compost is commonly prepared by mixing all organic wastes produced in agriculture with ash, fly ash, limestone, ground phosphates, etc. During aerobic destruction at a temperature of 45 to 60°C, the virulence of pathogens is killed or reduced.

The ratio between organic nitrogen and organic carbon is significant for the nitrogen mobility in soil. For organic substances stabilized in soil the C : N ratio is 20 to 30 : 1 (Jansson, 1958). If the ratio is higher than the above value, the nitrogen cycle shows its immobilization; when the C : N value drops under the above limit, mineralization occurs. The released NH_4 is utilized by heterotrophic microflora for protein synthesis, and oxidized to NO_3 through nitrification processes. Intensity of these processes depends on the soil water content and temperature and the quality of the soil organic matter whose composition affects the nitrogen cycle (the remineralized ammonium ion only is subjected to the nitrification process) and carbon cycle (in the nitrogen immobilization processes some other carbon substance are involved than during its mineralization).

The content of nutrients in each type of organic fertilizer can be seen in table 3.1.

Table 3.1. Content of organic fertilizers

FERTILIZER	DRY MATTER (%)	N (%) (TOTAL)	P ₂ O ₅ (%)	K ₂ O (%)	TRACE ELEM. (%)	OTHER SUBST. (%)
Solid Manure	25	0.4	0.2	0.5	1.4	organic matter 22.5
Liquid Manure	13.2	0.46 incl. 0.22 ⁺ (NH ₄)	0.09	0.52	0.34	organic matter 12
Slurry	9.2	0.4 incl. 0.19 ⁺ (NH ₄)	0.1	0.8	0.36	organic matter 6.9 - 7.8
Dung Water	2	0.25	0.005	0.5	0.13	see text
Straw	80 - 90	0.6	0.2	1.1	--	cellulose lignin hemicellu- lose
Compost	40 - 60	0.5	0.4	0.3	varies	organic matter 20

The effects of organic fertilizers on soil, and through the processes operating in the soil on groundwater quality, are evident.

The positive effects of organic fertilizers include the following:

- a) A higher proportion of organic matter and humus in the soil
- b) A higher content of biogenic (N, P, K, Ca, and Mg) and trace elements
- c) The soil is enriched with microorganisms essential for decomposition of organic matter and for making nutrients available to plants
- d) Better physical properties of soil (improved structure and ability to hold water etc.)
- e) A higher content of humus colloids resulting in improved adsorption capability of the soil
- f) A higher efficiency of inorganic fertilizers.

The negative effects of organic fertilizers on groundwater quality also include the following:

a) An increased need for inorganic nitrogen fertilizers in soil. This need arises particularly when fertilizing with harvest remnants with a high C : N ratio. When organic matter is added to soil, the soil bacteria proliferate enormously, consuming the available nitrogen which then needs to be supplemented by increased doses of inorganic fertilizers. Before a balance in the soil is restored, enormous nitrogen losses may occur due to leaching.

b) The physical properties of soil are disturbed by excessive doses of organic fertilizers containing a high proportion of water, such as liquid manure and slurry. Soil over-wetting combined with anaerobic processes can result in an imbalance of the soil nitrogen dynamics as a consequence of fundamental changes in microbial activity. The result is an increased leaching of nitrogenous substances. Another negative effect of soil over-wetting is that the soil humus is decomposed and its quality impaired as a consequence of the presence of more fulvic acids.

c) The chemistry of groundwater is directly affected by the application of organic fertilizers in liquid form containing ammonium nitrogen. This depends on the amount of manure applied, as well as soil, climatic and hydrogeological conditions.

d) Groundwater quality is directly affected by microorganisms present in organic fertilizers, particularly when raw animal faeces are applied without being subjected to thermal and anaerobic stabilization prior to application.

Table 3.2. lists the ways in which soil properties and groundwater quality can be negatively affected when organic fertilizers are used.

Table 3.2. Organic fertilizer effects on soil and groundwater quality

FERTILIZER	SOIL PHYSICAL PROPERTIES DISTURBED	SOIL MICROBIAL PROPERTIES DISTURBED	DIRECT GROUNDW. POLLUTION WITH N	DIRECT GROUNDW. POLLUTION WITH BACTERIA	HUMUS DEGRA- DATION
Solid Manure	-	-	-	-	-
Liquid Manure	+	-	+	-	-
Slurry	+	+	+	+	+
Dung Water	+	+	-	-	+
Green Manure	-	-	-	-	-
Straw	-	+	-	-	+
Compost	-	-	-	-	-

Legend: + negative impact
 - no negative impact

Of fundamental importance for studies of organic nitrogen dynamics in soil is the discovery, by Sauerbeck, of humus half-life decomposition. On the basis of experiments with various substrates with the isotope ^{14}C it has been found that individual types of humus formed from these substrates have different half-lives. Root and post-harvest remnants have a relatively short half-life (4 to 6 years), and so has liquid manure (about 5 years). The longest half-lives have been found with humus originating from various grass remnants. Some leguminous plants have half-lives as long as 25-30 years.

So far insufficient data have been collected for climatically and pedologically different regions. It is obvious that the time needed to stabilize a quantity of humus in individual types of agro-ecosystems is in the order of tens of years.

3.2.2. Biochemical degradation of organic fertilizers in soil

When organic fertilizers are applied, a complex biochemical degradation of organic matter takes place in soil. Depending on the depth of its storage, organic matter either putrefies or decays. These processes of degradation are affected by protein biocatalysts - enzymes, and microorganisms which decompose organic acids, sugar, starch, proteins, fats etc.

Decay of organic matter is an oxidizing process in the top soil layer without production of putrid gases. Putrefaction is characteristic of an anaerobic environment and is accompanied by the production of bad smelling substances and gases such as amines, mercaptan and hydrogen sulphide generated when sulphur-containing aminoacids are decomposed (e.g. cystine).

Products of both types of degradation (decay and putrefaction) are further degradable by enzymes of aerobic and anaerobic organisms.

Huge numbers of bacterial clones take part in the process of degradation (e.g. *B. saccharobutyricus*, *B. putrificus*, *B. vulgare*, etc.).

Some biocatalysts are mentioned below, which precondition the degradation of organic matter in farm fertilizers: amylase assists the degradation of starch, inulinase in that of inulin, cellulase and other cytases precondition the degradation of cellulose and hemicellulose, and esterase and phytase split esters and phytin to phosphoric acid and glycerol. Degradation of amine is controlled by amidase, and that of proteins by protease and pepsinase.

From the above it follows that when organic matter is destroyed, those biogenic and oligobiogenic substances which have been removed from the soil during biosynthesis of plant matter are returned to it. Degradation of manure, dung water and liquid manure releases into soil solution K^+ , NH_4^+ , NO_2^- , NO_3^- , S^{2-} , SO_4^{2-} , Cl^- , and PO_4^{3-} ions, microelements and complex organic compounds that form humus; microorganisms associated symbiotically with plants transform nutrients to an assimilable form which can be utilized by the next generation of plants.

When various types of composts are applied to soil, similar organic matter is introduced into soil, as in the case of farm fertilizers. The only difference is that the organic matter has been degraded earlier during maturation of the compost. Organic matter degradation during compost maturation takes place under increased temperature (up to 60°Celsius) which speeds up bioprocesses, while partial sterilization of the compost mass takes place. A number of dangerous microorganisms present in the faecal component of compost are destroyed by the increased temperature.

The mature compost mass therefore contains products of organic matter decomposition only - humus (humic and fulvic acids), which in turn contain nutrients and soil microorganisms.

Degradation of organic matter worked into soil by the ploughing of green vegetation proceeds in a way similar to that of farm fertilizers (destruction of cellulose, starch, sugar, amino acids and glycerids). However, processes connected with the degradation of faecal substances do not take place.

3.3. INORGANIC FERTILIZERS

Inorganic fertilizers have been used in farming since the last quarter of the 19th century. However, their mass-scale began after the second world war, i.e. after 1945. In the first decades of this century, Chile saltpeter (guano), phosphates and potassium salts were mined; later production of ammonium saltpeter and calcium saltpeter began. Since the 1940's fertilizers containing pure nutrients have been produced. Nitrogen content amounts to 30 per cent (saltpeter) or 48 per cent (urea). In the period from 1950 to 1975, the amount of annually applied nitrogen fertilizers grew approximately sixfold in most European countries (from 15.0 to 95.4 million tonnes). The percentage of the population dependant on the growth of cereal and other plant yields through the application of inorganic fertilizers increased from 10 per cent in 1910 to 40 per cent in 1970.

Compared with the high increase in the doses of nutrients supplied to soil by inorganic fertilizers, the growth of cereal yields is relatively slow (table 3.3.).

Table 3.3. Comparison of increasing doses of nutrients with wheat yields in some countries of the Northern Hemisphere.

COUNTRY	AVERAGE N,P,K DOSES IN kg. ha ⁻¹		AVERAGE WHEAT YIELD IN t.ha ⁻¹		INCREASE IN % FERTILIZERS YIELDS	
	1960	1976/80	1961/65	1980		
Netherlands	201	778.1	4.38	6.20	392.1	141.6
Belgium	200	499.0	3.70	4.61	230.5	124.6
Federal Rep. of Germany	148	471.4	3.31	4.89	318.5	147.7
Czechoslovakia	70	334.7	2.42	4.53	478.1	187.2
German Democratic Rep.	153	325.2	3.15	4.38	212.5	139.0
France	56	300.8	2.93	5.17	537.1	176.4
Hungary	24	262.4	1.86	4.76	1093.3	256.0
Austria	48	249.1	2.55	4.47	519.0	175.3
Un.Kingdom	59	239.6	4.04	5.88	406.1	145.5
Denmark	125	236.4	4.13	4.68	189.1	113.3
Poland	36.5	235.6	1.97	2.60	645.5	132.0
Bulgaria	28	198.4	1.81	3.98	708.6	219.9
Italy	39	170.1	2.01	2.69	436.2	133.8
US and Canada	15	98.7	1.70	2.25	658.0	132.4
USSR	5	80.9	0.96	1.60	1555.8	167.0

Potash, nitrogen and phosphate fertilizers are the most important inorganic fertilizers used in farming. After entering soil, they soon dissolve in water. Most nitrogen and potash fertilizers are highly soluble. Granulated and coated granulated fertilizers are soluble at a relatively slower rate. In multicomponent nitrogen fertilizers at least one of the components is slowly soluble.

Retention of nitrogen fertilizers in the plant root zone requires the use of coated (wax, sulphur) granulated and slow-acting fertilizers, as well as combined fertilizers of the N, P, K type (table 3.4.). The more expensive coated fertilizers are used predominantly in gardening.

Table 3.4. Slow-acting nitrogen fertilizers.

NAME OF FERTILIZER	N CONTENT IN %	PRODUCTION ON THE BASIS OF	NOTES
Ureaform carbamiform uramit nitroform	30 to 40	urea formaldehyde fertilizer	about 50 % N of slow solubility, amorphous dust
Z - urea	33 to 38	urea acetaldehyde fertilizer	about 40 % of less soluble N
CD - urea Floranid	30 to 32 28.2	urea croton aldehyde f.	90 % of slowly soluble N
IBDU f.	32 to 33	urea izobutyl aldehyde f.	solid; slow action
Oxamid	31.8	diamide oxalid acid produced of NH_3 and methane	granules applied in vegetation period
Urea coated with sulphur	32 to 37 N 13 to 30 S		active during vegetation period
Osmocote		$\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ and triazines	produced on the basis of magnesium-ammonium phosphate

Phosphate fertilizers are produced by refining raw phosphates to superphosphates. Their solubility is low, and they adsorb well in the soil. Their vertical migration is in the order of millimeters per year.

In areas with soil erosion, phosphorus adsorbed to soil particles is transported to surface water and causes its eutrophication. Fluorapatite is a common addition in phosphates and superphosphates (2.0 to 4.2 per cent), from which fluorine is released into soil, plants and in a small quantity also to groundwater. Over a period of 30 years, fluorine content in arable land has doubled due to the application of phosphate fertilizers. Transport of fluorine into the environment (caused by the application of fertilizers and from other sources) shows a constantly rising trend:

in 1950 -	0.1×10^6	t
1970 -	4.1×10^6	t
1980 -	6.9×10^6	t

As a result also trace elements like Cd come into the environment. Potash fertilizers (especially the K^+ cation) adsorb well in soil. The need for potassium in protein synthesis has resulted in increasing doses of potash fertilizers. In this way the K : Na ratio has changed for the benefit of potassium, especially in fodder plants, and also in cereals. As a result of fertilizing, an increased content of potassium can be observed, and a simultaneous decrease of sodium and calcium content in surface water also. On the other hand, until now no increased potassium content in groundwater has been reported. Other inorganic fertilizers containing calcium, magnesium, cobalt, molybdenum and other biogenic and trace elements are also being used. Lime and gypsum are used to a great extent for reducing soil acidity. Magnesium is an important component of chlorophyll, and in sufficient amounts also affects enzymatic reactions. Calcium is an important building element of protoplasmic structure.

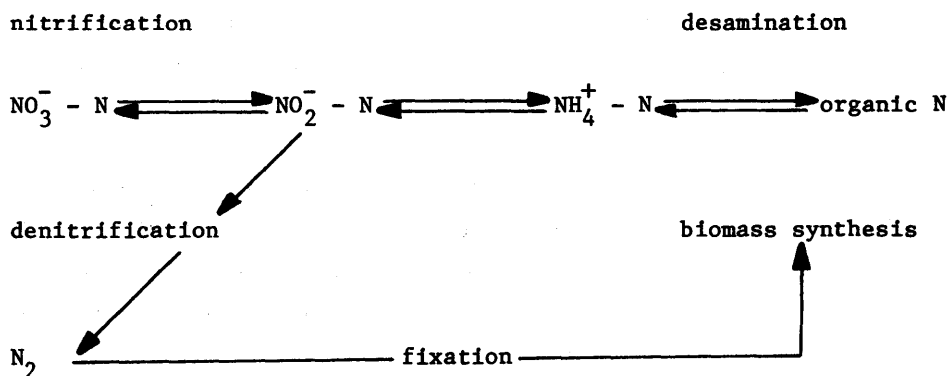
3.3.1. Chemical decomposition of fertilizers

Inorganic fertilizers in soil are subjected to decomposition in the form of dissociation in water solutions and are less easily adsorbed to the soil complex. The ability to decompose varies with different types of fertilizer. The original chemical components are transformed by decomposition into others with different properties. Decomposition is caused by chemical reactions, themselves affected by microorganisms and biochemical activity.

In potash fertilizers the potassium cation is mostly bound to the soil complex; chlorides are not transformed and sulphates in anaerobic conditions are biochemically reduced to hydrogen sulphide. Additionally, they enter into a dual reaction, and reach equilibrium with calcium bicarbonate.

Nitrogen fertilizers in an acidic medium release nitrogen as NO_3^- ; in neutral and alkaline media intake of nitrogen by plants takes place at the same time, in the form of the ammonium ion - NH_4^+ . At lower temperatures the release of nitrate drops, to the detriment of the ammonium ion.

Inorganically bound nitrogen can be in the form of ammonium, nitrite or nitrate. Each of the oxidation forms in soil and water are controlled predominantly by biochemical processes. The circulation of nitrogen in water can be represented as follows:



The greater part of the circulation is based on oxidoreduction reactions controlled by the relevant bacteria and the oxygen regime.

Oxidoreduction processes in the unsaturated zone of the rock environment preclude, or repeatedly replace, each other.

Nitrification is oxidation of ammonia-form nitrogen by nitrifying autotrophic bacteria, under aerobic conditions to nitrites and in turn to nitrates. During oxidation of $\text{NH}_4^+ - \text{N}$ to $\text{NO}_3^- - \text{N}$ hydrogen ions are released, resulting in a drop of pH.

Nitrogen occurs in water mostly as the ion NO_3^- . Since nitrates have a variety of sources, are easily soluble and are not sorbed, they cause groundwater quality to deteriorate. A continuous increase in nitrate concentrations is observed during long-term monitoring of groundwater chemical compositions (Cherry et al., 1984).

Except for biochemical nitrification, the ammonia-form N does not oxidize in soil and aquifers. From the standpoint of reducing NH_4^+ mobility, the ion exchange reaction with colloid inorganic and organic soil particles is essential.

Nitrites are unstable in water: they oxidize easily, or they are chemically and biochemically reduced.

Nitrates are only stable in an aerobic environment and they migrate easily in any type of soil. Except for the above-mentioned denitrification, they are not subject to any other decomposition and are an important oxidizing agent of organic matter present in water.

Denitrification is the reduction of nitrites and nitrates to ammonia and to elementary nitrogen which volatilizes into the soil atmosphere. The process requires strictly anaerobic conditions or a concentration of less than 0.5 mg of O_2 per liter in water and is affected by microbes.

Denitrification tends ameliorate the impact of nitrate inputs to groundwater. According to Lindsay (1979) and Cherry et al. (1984), denitrification can be expected to occur only in zones that are devoid of dissolved oxygen. Field studies have proved that denitrification will occur in zones with low but measurable concentrations of oxygen where organic matter and denitrification bacteria exist (Gillham and Cherry, 1978; Cherry et al., 1984). Nitrates are reduced in porous micro-environments or on grain surfaces where conditions for reduction exist.

As the result of phosphate fertilizers application soil contains undissolved phosphates of Ca, Mg, Fe and Al, which are chemically fixed to the soil, or sorbed in it. The dissolved part of phosphate fertilizers contains simple or complex forms of orthophosphates and polyphosphates. Catenary polyphosphates fix various cations into complexes and preserve them in the dissolved form, otherwise they would form insoluble salts with some anions. The equilibrium concentrations of phosphates in groundwater in neutral and alkaline media are given by the solubility of hydroxylapatites $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. Phosphates are in this way eliminated from water. Depending on the presence of bicarbonates, phosphate ions are again released into solution. Phosphates, and above all polyphosphates, create complexes with cation and other ligands (sulphates, carbonates and fluorides), which increases phosphate solubility in water. Polyphosphates are chemically hydrolyzed to orthophosphates, although very slowly; biochemical hydrolysis is, depending on the content of microorganisms, faster.

Phosphates act as buffers, in a solution they are present in an equilibrium ratio of PO_4^{3-} , HPO_4^{2-} and H_2PO_4^- , while parts of the latter are conditioned by H^+ concentration.

Compounds of Fe are released into solutions by a number of chemical and microbial processes. Similarly, circulation of sulphur also depends on physicochemical and microbial processes.

The principal amount of Ca^{2+} and Mg^{2+} is supplied when soil is limed. In order to maintain soil reaction at the optimum value of pH 6 to 7, doses of 100 to 200 kg of CaCO_3 or CaO per hectare are required. Under these conditions, about 70 per cent of the supplied calcium is fixed in the complex of humus and clay minerals. Ten to fifteen percent of cations are in the form of NH_4^+ and H^+ , and ten to fifteen per cent as chelates of Mg^{2+} and K^+ , including microcomponents and trace elements. Of the amount of CaCO_3 and CaO supplied; nearly 40 per cent is used to neutralize effects of acid fertilizers, and 10 to 30 per cent to compensate acid fallout. The rest replaces losses caused by the removal of crops.

3.3.2. Impact of physical and chemical properties of inorganic fertilizers on groundwater quality.

The physical and chemical properties of inorganic fertilizers which affect groundwater quality are listed in table 3.5. The most important characteristics of fertilizers are described in columns 1 to 8. Solubility (column 1) is expressed as the amount of water (in liters) and time (in hours) needed to dissolve 50 grammes of a fertilizer. Most nitrogen fertilizers are moderately to very soluble. The least soluble of saltpeters is calcium nitrate, followed by ammonium sulphate and nitrogenous lime. Granulated and coated granulated fertilizers dissolve for a longer period of time than pulverized fertilizers. A separate class of fertilizers comprises multi-component nitrogen fertilizers; at least one of their components is usually slowly soluble. In aqueous solutions of fertilizers, chemical substances are dissociated to ions. In this form they migrate or are sorbed, and they are subjected to other chemical and biochemical processes. Solubility is the primary property preconditioning the generation and concentration of components in groundwater.

The equivalent of acidity or alkalinity (column 2) is used for nitrogen fertilizers and is expressed as the amount of CaO (in grammes) theoretically needed to neutralize a physiologically acidic fertilizer, or the amount of CaO needed to make alkaline an environment in cases when physiologically basic fertilizers are used. Acidity or alkalinity of fertilizers affects only marginally the pH of water.

Hygroscopicity (column 4) is expressed as the hygroscopic point (equilibrium relative humidity over saturated solutions of salts), i.e. the ratio of water vapor tension over a humid substance and pure water at a given temperature. A fertilizer dissolves or dehydrates proportionally to the amount by which the hygroscopic point differs, plus or minus, from the relative humidity of air. Hygroscopicity greatly affects the caking of fertilizers; hygroscopic fertilizers dissolve more easily in water.

Adsorption capability (column 5) cannot be expressed as a numerical value. This capability comprises the chemical, physicochemical and biological adsorption in the soil complex. Neither chemical nor

physical sorption of nitrate ions occur with the nitrogen fertilizers; their adsorption is only biological. The NH_4^+ , Na^+ , K^+ , and Ca^{2+} cations sorbe well into the soil complex, while during their adsorption, other ions are also displaced. Of the soluble portion of phosphorous fertilizers, strong cations are chemically adsorbed. There is also a partial physicochemical adsorption of anions. Adsorption of the chloride ion does not occur with potassium fertilizers. Sulphates can be chemically adsorbed while forming poorly soluble or insoluble salts with some cations (Ca, Mg). Thus only potassium is adsorbed into some soil types via ion exchange, although it can also be leached into groundwater.

Resistance of fertilizers in soil (column 6) depends on their solubility and adsorption capability as well as their rate of dissociation. Mobility (column 7) in soil differs for the cation and anion components of a fertilizer and is also affected by its solubility and adsorption capability. Mobility of nitrates and chlorides is high, and that of ammonium cations and ammonia low. Adsorption, as well as resistance and mobility of fertilizers in soil determine the degree to which the quality of groundwater is affected in terms of time and space.

Decomposition (dissociation or degradation) of fertilizers in soil (column 8) is the process of transformation of the initially-applied components into other substances possessing different physical and chemical properties. Reactions can be chemical or biochemical. Chemical reactions of nitrogen fertilizers are mostly reduction processes, for the greater part combined with biochemical degradation; oxidation and reduction are affected by bacteria. Potassium and phosphorous fertilizers in solution enter chemical reactions.

The ability to decompose varies with different inorganic fertilizers. Decomposition of fertilizers particularly affects groundwater quality.

The possibility of water, especially groundwater (column 9) toxification is brought about by the property of inorganic fertilizers to transport harmful or toxic substances into water; it results from all the above-mentioned properties. Water toxification can be either direct (toxic elements or through ions being released during ferti-

TABLE 3.5. Physical and chemical impact of fertilizers on groundwater quality

Industrial Fertilizers	1 Solubility* l(H ₂ O) hour	2 Equivalent of Acidity (-) and Alkalinity (+) g/kg	3 Specific Weight t . m ⁻³	4 Hygroscopicity* 20°C 30°C	5 Adsorption capacity
NITROGEN FERTILIZERS					
Calcium nitrate	5.09 121.2	+ 12	0.9-1.1	55.4 46.7	low, only Ca ²⁺
Ammonium saltpetre	enorm.solub.	- 41	0.82	66.9 59.4	partial, only NH ₄ ⁺
Sodium saltpetre	well soluble	+ 16	1.1-1.4	77.1 72.4	low, only Na ⁺ ,
Potassium saltpetre	well soluble	- 13	-	92.3 90.5	low, only K ⁺
Ammonium saltpetre with limestone	5.18 121.0	- 13	1.0-1.15	63.9 69.1	increased NH ₄ ⁺ and Ca ²⁺
Ammonium sulphate	4.40 104.8	- 63	0.83-0.9	81.0 79.2	partial, only NH ₄ ⁺
Liquid ammonia	well soluble	- 83	0.62	- -	well NH ₄ ⁺
Ammonium water	-	- 20	0.9-0.98	- -	partial NH ₄ ⁺
Urea	0.15 3.57	- 46	0.67-0.7	80.0 72.5	partial NH ₄ ⁺
Nitro-lime	6.59 156.9	+ 63	0.6	- -	
Urea (50%)+ammonia (50%)		- 30	1.30	- -	partial NH ₄ ⁺
N content=390 g/l					
PHOSPHORUS FERTILIZERS					
Superphosphate I	2.34 55.7		1.2	- -	
Granulated super phosphate	8.89 221.6		1.1	94.1 73.7	
Tri-superphosphate	9.2 240.6		1.0	94.1 93.7	
Pulverized phosphates	4.12 98.1		1.2-1.7	- -	
Thomas' powder	insoluble		2.0-2.2	- -	
Simple superphosphate + raw phosphate	2.84 67.6		-	- -	
POTASSIUM FERTILIZERS					
Potassium chloride 40% 50%	2.48 591.2		1.0-1.2	71.2 69.4 74.6 69.9	low only K ⁺
Potassium chloride + magnesium sulphate	31.0 739.3		1.0	71.2 68.1	
Kainit	24.3 578.3				
Potassium sulphate	6.82 162.3	potentio- nally acid	12.0-14.0	98.5 95.3	low, only K ⁺
Combined NPK 1	14 334		0.91-1.1	67.8 63.8	increased

* units see chapter 3.3.2.

6	7	8	9	10
Resistance	Mobility in Soil cat. anion.	Decomposi- tion chem.bioch.	Possibility of Water contami- nation cat. anion.	Other Properties
low	low high	+	(NH ₄ ⁺) NO ₃ ⁻ , NO ₂ ⁻	Na ⁺ negatively affects physical properties of soil
low	low high	+	NH ₄ ⁺ NO ₃ ⁻ , NO ₂ ⁻	
low	low high	+	(NH ₄ ⁺) NO ₃ ⁻ , NO ₂ ⁻	
low	low high	+	(NH ₄ ⁺) NO ₃ ⁻ , NO ₂ ⁻	
middle	low high	+	NH ₄ ⁺ NO ₃ ⁻ , NO ₂ ⁻	
low	low middle	+	NH ₄ ⁺ -	
low	low high	+	NH ₄ ⁺ NO ₂ ⁻ , NO ₃ ⁻	corrosive effects, volatile
low	low high	+	NH ₄ ⁺ NO ₃ ⁻ , NO ₂ ⁻	contains some detriments (phenols, cyanamides)
extremely low	low high	+	NH ₄ ⁺ NO ₃ ⁻ , NO ₂ ⁻	contains the toxic biuret and volatile NH ₃
extremely low-low	low high	+	NH ₄ ⁺ NO ₃ ⁻ , NO ₂ ⁻	the decomposition product, cyanamide, is toxic
extremely low	low high	+	NH ₄ ⁻ NO ₃ ⁻ , NO ₂ ⁻	corrosive effects, point of soli- dification -10°C
high	extremely low	+	HPO ₄	
		+	HPO ₄	
		+	HPO ₄	
		+	HPO ₄	
		+	HPO ₄	
		+	HPO ₄	
low, only potassium stays in soil for 2-3 years	low high	reaction of ion exchange	(K ⁺) Cl ⁻	
	low high		(K ⁺) Cl ⁻	
	low high		(K ⁺) Cl ⁻	
	low middle		(K ⁺) Cl ⁻	
higher	low high	+	(K ⁺) NO ₂ ⁻ , NO ₃ ⁻ , HPO ₄	

lizer reactions in the soil complex - they are then transported into water), or indirect (toxic components are released in an underground aquifer or in a stream as a result of reactions between fertilizers and water).

3.3.3. Biological adsorption of fertilizers and its impact on groundwater quality

Apart from the physical and chemical properties of fertilizers, the biological transformation of nitrogen fertilizers has special importance for groundwater quality. Fertilizers directly affect the degree of biological adsorption by the roots of cultivated plants, as well as the numbers and kinds of symbiotic microorganisms living on these roots. With the growing availability of nutrients provided by fertilizers for plant roots, the amount of nutrients leached into groundwater decreases.

Biological transformation of fertilizers occurs intensively in the soil layer of arable land in the root zone.

The thickness of the root zone of field-grown plants can extend to 3 meters below surface, its center of concentration extending to 0.6 meters.

Biological processes may be subdivided thus:

a) Root adsorption of nitrogen fertilizers into plants.

Nitrogen fertilizers applied to the surface of fields (vegetation) dissolve in precipitation water and permeate into the soil solution to reach plant roots. Plants accept nitrogen from fertilizers, dissociated to ions. The basic movements in soil pores are diffusion and capillary, their intensity growing with the increasing soil water content. Plant root hairs accept the NO_3^- and NH_4^+ ions in the process of mechanical as well as selective diffusion connected with electro-osmosis. In this an important role is played by transpiration from the surface of plant leaves, which results in an under-pressure suction of water containing nutrients. From the groundwater protec-

tion viewpoint, those plants which transport the maximum proportion of nutrients into their above-soil parts are the most effective. The greatest amount of nitrogen is required by plants in their early stages of development, and therefore groundwater with minimal pollution is found under grassland and pastures, although these may be highly fertilized with nitrogenous compounds.

However, the root adsorption of plants is commonly accompanied by microbial symbiotic adsorption.

b) Transformation of nitrogen fertilizers into microorganisms. Part of nitrate fertilizers is transformed into cell walls of microorganisms (bacteria, actinomycetes and algae) especially in the rhizosphere, i.e. a 0.1 to 0.3 mm thin layer of soil surrounding root hairs.

The ability to fixate air nitrogen is possessed by microorganisms living in symbiosis on the roots of leguminous plants (Rhizobium, Anabaena, Nostoc, Nostocales, etc.), independent bacteria (aerobic Axotobacter, anaerobic Clostridium), photosynthetic bacteria and some soil bacteria similar to pseudomonades.

The quantity of nitrogen fixated by free microorganisms is reported to amount up to $10 \text{ kg} \cdot \text{ha}^{-1}$ per year, while the quantity of nitrogen fixated by symbiotic microorganisms is an order higher.

Table 3.6. Approximative quantities of nitrogen (N_2) fixed under ideal environmental conditions.

PLANT/CONDITIONS	AMOUNT OF N_2 FIXED EACH GROWING SEASON, $kg \cdot ha^{-1}$
<u>Legumes (symbiotic)</u>	
Alfalfa	225
Red Clover	130
Soybean	110
Cowpea	100
Bean	45
<u>Nonlegumes (symbiotic)</u>	
Alder, red	170
Casuarina	60
Sweet gale	10
<u>Nonsymbiotic</u>	
Soil underpines	45
Bare soil in tropics	125
Regenerated African Bush	720

Source: Donahue, R.L.; Miller, R.W.; Shickluna, J.C. (1977).

c) Transformation of nitrogen fertilizers into macroorganisms. Macroorganisms affect positively the composition of soil organic matter, resulting in increased soil and biological adsorption of inorganic fertilizers. On the other hand, fertilizers transport in the upper part of the unsaturated zone is affected adversely by macroorganisms, because they are involved in the generation of preferential flow paths.

3.3.4. Circulation of other nutrients

Circulation of sulphur differs from that of nitrogen in that plants are able to accept it in the form of SO_4^{2-} which they reduce to hydrogen monosulphide and use to build proteins. The latter are in turn directly usable by animals. When plant matter decays, the hydrogen monosulphide is microbially oxidized back to form SO_4^{2-} which is assimilated by the plant root system. Part of the sulphur is assimilated by microorganisms and fungi in the form of SH^- .

Phosphorus is assimilated by plants in the form of the PO_4^{3-} ion. In this process it is fixed in the form of nucleoproteids, lecithin and phytin. Unlike plants, living organisms are able to make use of inorganic phosphates, a large proportion of which they return in wastes.

Potassium as a nutrient is used mainly as an element essential for metabolism and for NO_3^- assimilation. Mg^{2+} , Ca^{2+} and Na^+ are used for building plant tissues. Fe^{3+} and Mn^{4+} are also essential, and plants assimilate these to a specific degree. The release of Fe from primary minerals into solution is partly carried out by ferrous bacteria which oxidize Fe^{2+} to Fe^{3+} , and some moulds (Cytromyces).

The release of the above nutrients into solution depends on the presence of water in the soil layer, and is considerably influenced by the content of humus and clay minerals.

3.4. PESTICIDES

The term pesticides here includes herbicides, insecticides, fungicides, miticides and others.

The beginnings of phytopharmacy, the science of plant behavior and control of plant pests, date back to the 19th century. However, the protective action of some inorganic salts and substances was known earlier (for example, sulphur was used against insects and mites as early as the Middle Ages). At the beginning of this century, the use of mercury and arsenical compounds became widespread. In the 1930s production of dinitrocreosol increased. After 1945, the application of pesticides increased rapidly with the use of compounds such as DDT and its derivatives HCH, heptachlor, lindane, aldrin, dieldrin, etc. In the 1980s carbamates, derivatives of urea, carboxylic acids, and biochemicals with a wide range of action began to be used.

At present more than 32,000 different pesticide compounds are being used in agriculture containing some 1,800 active ingredients.

Most pesticides are substances with a low molecular weight and low solubility in water. They move in the soil by capillary transport, and in a water solution by molecular diffusion.

Adsorption/desorption of pesticides in soil colloids is affected by the following factors: the chemical composition, shape and configuration of the pesticide molecule, its acidity or alkalinity (denoted as pK_a or pK_b), solubility in water, distribution of electric charges on cations, molecule polarity and the size and polarizability of the molecule.

Table 3.7. lists the most important factors affecting the adsorption of each type of pesticide and their likely impact on groundwater quality.

Column 1:

Depending on their chemical nature, pesticides are classified into two groups - ionic and nonionic pesticides. The two groups differ substantially in their adsorption capability, which directly affects the mobility of the pesticides in soil and water environments. Ionic compounds can be classified as cationic, acidic, basic and miscellaneous.

TABLE 3.7. Factors affecting adsorption of selected groups of pesticides and their leaching into groundwater

1	2	3	4	5	6	7	8	9	10	11
Chemical Group	Adsorption Mechanism	Adsorption Organic Matter	Adsorption to Clay Minerals	Bond to Organic Matter	Clay Minerals	Soil pH Effect	Soil Water Content Effect	Solubility in Water at 20 - 25°C	Persistence in Soil (Half-life) in days	Soil Mobility
I										
1. Ionic Pest.					very		positive			
1. Cationic Pest.	e/d/g	+ d/	+ e/d	strong	strong	small	small	high	4000 - 5000	1
2. Acidic Pest.	f/g	+	-	weak	very weak	> pK _a	positive	high at greater pH	10 - 140	4.5
3. Basic Pest.	c/d/e/f/g/	+ c/d/e/f/	+ d/e/	weak	medium	< pK _b	considerable			
							positive	high at lower pH	25 - 400	2.3
							medium			
4. Miscellaneous Ionic Pest.	g/	+	-	weak	almost none	varies	positive		170 - 350	4.5
							considerable			
							high			
II										
5. Chlorinated Hydrocarbons	a/b/d/	+ a/d/	+	very strong	weak	none	positive	low	460 - 1650	1
							small			
6. Organophosph.	a/b/c/d/e	+ b/d/	+ c/	very strong	medium	< 7	positive	considerable	0.9 - 60	1
							small			
7. Substituted Anilines	a/b/d/	+ b/d/	+	strong	weak	none	considerable	low	45 - 180	1
							negative			
8. Phenylureas	a/b/c/d/f/	+ b/d/	+ c/f/	medium	weak	< 7	considerable	low to medium	120 - 400	2.3
							pos., consid.			
9. Phenylcarbamates and Carbamates	a/b/c/d/	+ b/d/	- c/	medium	weak	< 7	positive	considerable	10 - 70	2.3
							considerable			
10. Amides	a/b/d/	+ b/d/.	-	weak	very weak	none	pos., medium	medium	30 - 70	3
							pos., medium			
11. Thiocarbamates Carbothioates	a/b/d/	+ b/d/	+	strong	medium	none	positive	medium	30 - 220	2
							considerable			
12. Acetamides	a/b/d/	+ b/d/	-	strong	weak	none	pos., medium	medium	300 - 400	2
13. Phenylamides	a/b/d/	+ b/d/	+	strong	medium	none	pos., medium	medium	60 - 180	2
							pos., medium			

Column 2: a/ Van der Waals attractions

b/ Hydrophobic bonding

c/ Hydrogen bonding

d/ Charge transfer

e/ Ion exchange

f/ Ligand exchange

Column 3,4: + adsorption exists

- adsorption low or none

Column 7: pH effect understood in the sense of

adsorption increase

Column 8: Soil water content understood in the

sense of adsorption increase

Column 11: 1 = immobile pesticides

2 = poorly mobile pesticides

3 = mobile pesticides

4 = highly mobile pesticides

5 = extremely mobile pesticides

The cationic pesticides (for example paraquat, diquat) are compounds with a high solubility in water which ionize in aqueous solutions to form cations. In solutions, they exist as divalent cations and positive charges are distributed around the molecules.

The acidic pesticide groups includes preparations with carboxylic or phenolic functional groups which ionize producing organic anions (for example 2,4-D, MCPA, mecoprop, dichlorprop, 2,4,5-T, etc.).

Basic pesticides such as s-triazines and triazoles behave in water solutions as weak bases. They associate with hydrogen ions producing protonated species that can be adsorbed onto a negative site of a soil colloid. Miscellaneous ionic pesticides such as bromacil, terbacil and oryzalin have a slightly acidic or basic character. Their molecules contain certain atoms or functional groups which result in these compounds having different properties than the cationic, basic or acidic pesticides.

Nonionic pesticides differ substantially in character. Their adsorption to soil colloids depends chiefly on the chemical properties of the compounds comprising the soil adsorption surfaces involved.

The group of nonionic pesticides includes chlorinated hydrocarbons, organic phosphates, substituted anilines, phenylureas, phenylcarbamates and carbamates, amides, thiocarbamates, carbothioates, acetamides, phenylamides and benzonitriles.

The chlorinated hydrocarbons (group 5) with the exception of lindane are practically insoluble in water. Apart from DDT this group includes endrin, aldrin, lindane, heptachlor etc.

The organophosphates (group 6), are more soluble than the chlorinated hydrocarbons and under normal conditions decompose very quickly.

The phenylureas (group 8) include linuron, monuron, chlortoluron, neburon etc. Within this group there are considerable differences in adsorption which depend on the quantity of the halogenic substituents on the phenolic ring and their solubility.

The phenylcarbamates and the carbamates (group 9) are water soluble insecticides or herbicides (i.e. protham, carbaryl), but of only moderate mobility in the soil environment.

The amides (group 10) are medium-soluble compounds with a low adsorp-

tion ability, for example alachlor, propachlor.

The thiocarbamates, the carbothioates and the acetamides (group 11) include compounds such as aldicarb, EPTC, vernolat, pebulat, cycloate, etc. Adsorption of these preparations depends on the content of organic matter in soil.

The phenylamides (group 12) are herbicides. Adsorption is generally irreversible being largely controlled by the soil organic content.

The benzonitriles (group 13) include for example dichlobenil. Adsorption is strong and movement through soil very limited (Khan, 1980).

Column 2.

The following factors play a role in adsorption:

a) Van der Waals attractions - especially when nonionic and nonpolar molecules or their parts are adsorbed (picloram, carbaryl, parathion). (Leenheer and Ahlrichs, 1971)

b) Hydrophobic bonding-nonpolar pesticides are adsorbed to hydrophobic regions of soil organic matter (DDT, phenylureas), (Hance, 1969).

c) Hydrogen bonding is the principal mechanism for adsorbing polar nonionic molecules to clay minerals and s-triazines to organic matter. A hydrogen atom forms a bridge between two electron-negative atoms. (Hadzi et al., 1968).

d) Charge transfer is a bonding where electrons are transferred from donors to electron acceptors; this bonding occurs when s-triazines are adsorbed to the soil organic matter and clay minerals. (Hayes, 1970, Haque et al., 1970).

e) Ion exchange occurs with pesticides which exist as cations or which are positively charged due to protonation (paraquat, diquat).

f) Ligand exchange is the type of adsorption when one or more ligands are replaced by a molecule of the adsorbent, for example when s-triazines are adsorbed to transition metals in humic acids, ureas to clay minerals, etc.

g) Direct and induced ion-dipole and dipole-dipole interactions between molecules of water. The energy of interaction between H^+ and H_2O supports adsorption of polar and ionic organic pesticides.

Columns 3 and 4.

The adsorption of pesticides in soil is mostly controlled by the quantities and the type of organic matter and clay minerals in that soil. When considering pesticide mobility, adsorption from solution is the most important. The ability of pesticides to adsorb to different adsorbents is derived from adsorption isotherms of various types depending on the pesticides affinity to the adsorbent. The process of pesticide adsorption is affected by the following factors:

- a) Character of functional groups
 - b) Character of substituting groups
 - c) Position of substituting groups
 - d) Presence and magnitude of unsaturation in the molecule
- (Bailey, White, 1970).

At normal to medium concentration of pesticides in solution, adsorption is expressed by the equation

$$x/m = K C^n$$

where x/m is the adsorbed quantity per unit weight, K is a constant, and C is the concentration of the pesticide in the solution when equilibrium has been reached.

The value of K converges to that of K_d , where

$$K_d = \frac{\mu\text{g of adsorbed pesticide to g of adsorbent}}{\mu\text{g of dissolved pesticide to g of solution}}$$

after equilibrium of the solution has been reached. When organic carbon is the adsorbent, $K_d = K_{oc}$. In the following table (3.8) K_{oc} values for some pesticides are listed.

Table 3.8. Coefficient of adsorption (K_{oc}) for some pesticides

PESTICIDE	K_{oc}
24-D	32
monuron	83
simazine	135
propazine	152
chlorpropham	245
diuron	485
prometryne	513
chloroxuron	4 986
DDT	243 000

(Hamaker et al., 1972)

K_{oc} values can be used to express the pesticides ability to adsorb to any soil when the organic carbon content of that soil is known.

Columns 5 and 6.

The degree of adsorption to organic matter or onto clay minerals depends on the character of the adsorbent and the pesticide's physical and chemical properties. The importance of the different bonding mechanisms to adsorption is shown in columns 3 and 4, table 3.7.

Column 7.

Effect of soil pH on pesticides adsorption depends on the chemical nature of pesticides and on the type of bonding involved. Hydrophobic bonding is essentially independent of pH; hydrogen bonding is limited to acidic media. The maximum adsorption of s-triazines is at pH 7. The acidity of soil colloids affects the creation of the protonated molecules of adsorbed basic pesticides during ion exchange. The soil colloid's pH may be as much as two units lower than the soil solution pH. Protons of basic pesticides are created even when water pH is higher than 7. (Weber, 1972).

Column 8.

Soil water content affects pesticide adsorption and solubility. A higher soil water content usually increases adsorption, since pesticides are adsorbed mostly in the liquid phase. When the soil water content declines, compounds crystallize and adsorption is very limited. Cationic herbicides are an exception since they are strongly adsorbed at all values of the soil water content. For most pesticides the relative soil water content is important: if it exceeds 30 per cent, the adsorption generally decreases rapidly and diffusion predominates.

Column 9.

Solubility in water is one of the indicators of pesticide adsorption. Generally within a particular chemical group the extent of pesticide adsorption is directly related to its solubility in water, and is controlled by it.

The hydrophobic character of pesticides increases with the decline in their solubility, while their adsorption to soil colloids increases. Therefore, an indirect relation exists between their solubility and adsorption. Some s-triazines and substituted ureas are an exception, when a direct relation exists between their solubility and adsorption to clay minerals (Weber, 1972).

Column 10.

The persistence of pesticides in soil depends on their technological preparation, the manner of their use, climatic conditions, bacterial inoculum of soil and the type of plant on which the pesticides have been applied. Data listed in the table are therefore relative. Data on the persistence and mobility of pesticides are important when considering their impact on groundwater quality. For example, s-triazines are moderately mobile but due to their considerable persistence they may become a source of groundwater pollution.

Column 11.

Impact on groundwater quality is differentiated according to the solubility of the pesticides in water, their strength of adsorption

to soil colloids, and their mobility. According to their mobility, pesticides can be classified into one of the following five categories:

1. immobile
2. poorly mobile
3. moderately mobile
4. highly mobile
5. extremely mobile.

Within each category, the pesticides are ranked in estimated decreasing order of their mobility:

1. neburon, chloroxuron, DCPA, lindane, phorate, parathion, disulfoton, diquat, chlorphenamide, dichlormate, ethion, zineb, nitralin, TH 1568 A, morestan, isodrin, benomyl, dieldrin, chloroneb, paraquat, trifluralin, benefin, heptachlor, endrin, aldrin, chlordane, toxaphene, DDT.
2. siduron, bensulide, prometryn, terbutryn, propanil, diuron, linuron, pyrazon, molinate, EPTC, chlorthiamid, dichlobenil, vernolate, pebulate, chlorpropham, azinphosmethyl, diazinon.
3. propachlor, fenuron, prometone, naptalam, 2,4,5-T, terbacil, propham, fluometuron, norea, diphenamid, thionazin, endothall, monuron, atratone, atrazine, simazine, ipazine, alachlor, ametryne, propazine, trietazine.
4. picloram, fenac, pyrichlor, MCPA, amitrole, 2,4-D, dinoseb, bromacil.
5. TCA, dalapon, 2,3,6-TBA, tricamba, dicamba, chloramben.

The greatest danger of pesticide transport into groundwater exists in irrigated areas. However, due to adsorption, the pesticide concentration in groundwater rapidly decreases.

When pesticides occur at high concentration in groundwater, caused perhaps by leakage from discarded insufficiently emptied containers, the adsorption of some of these pesticides occurs according to the nonlinear Freundlich isotherm (Davidson et al., 1976, 1980; Cherry et al., 1984).

Repeated applications of highly mobile pesticides such as the derivatives of carboxyl acids is potentially hazardous to groundwater. The chemistry of these substances rapidly changes in the soil and rock environment. The products of transformation can, however, affect the organoleptic properties of water, even at concentrations markedly lower than the Acceptable Daily Intake (ADI).

With some exceptions the ADI values have not been established for pesticides and at present it is not known precisely what pesticide concentrations are critical for the human organism. The available values for the highest permissible pesticide concentrations in water are mostly speculative. Data on the chronic effects of pesticides on the human organism are also not available. Until ADI values are known, medical experts will consider even the least concentration of pesticides in drinking water to be of consequence.

Pesticide toxicity is expressed as values of LD_{50} and LC_{50} . The coefficient Q is being introduced and is calculated on the basis of the LC_{50} value and the amount of pesticides needed per m^2 of treated area. This coefficient is used to assess the relative dangers of pesticides for living organisms. Pesticides with Q less than 5 are considered dangerous (Table 3.9.).

Table 3.9. Assessment of acute toxicity of some pesticides for birds

ACTIVE INGREDIENT	LD ₅₀ mg PER kg OF BODY WEIGHT	LC ₅₀ mg PER kg OF BODY WEIGHT	COEFFICIENT Q
Toxaphene (camphechlor)	260	685	1.7
Fenitrothion	55.6	440	2.0
DNOC	9.6	630	3.5
Methyl-parathion	10.0	751	1.4
Dichlorvos	11.3	298	5.0
Mevinphos	6.0	204	11.0
Endosulfan	16.8	1250	12.0
Lindane	210	425	24.0
Carbaryl	1660	5000	40.0
Atrazine	2000	5000	7
Chlorpropham	2000	5000	12
Diquat	560	1346	13
2,4-D	668	5000	22
Simazine	--	5000	20

(Grün et al., 1982)

3.4.1. Chemical decomposition of pesticides

The behavior of the most important groups of pesticides in various environments is the result of chemical reactions, physical phenomena and biological processes:

- Chloracetamides, dinitroanilines, thiocarbamates and chlorinated hydrocarbons (DDT, lindane), evaporate into the atmosphere to a great extent. Depending on soil water content, temperature, wind and vapor pressure, between 5 and 50 per cent of these substances evaporate into the air. Evaporation takes place from large areas of chemically treated vegetation or soil. These compounds are therefore present in the atmosphere and can enter the groundwater as a result of precipitation, especially where infiltration rates are rapid. (Foy, 1975; Guenzi, 1975).

- Pesticide persistence in soil is affected by evaporation, adsorption, leaching by water and decomposing reactions. Pesticides whose decomposition or evaporation is slower than their movement in soil are dangerous for groundwater. (Vročinskij, 1979; see factors listed in comments to column 10 in table 3.7.).

- Pesticides in soil are transformed by chemical, photochemical and biochemical reactions. Chemical reactions such as oxidation, reduction, hydrolysis, elimination of radicals and isomerization are often supported by enzymes that act as catalysts. Photochemical reactions occur on soil surfaces under the influence of solar radiation. Biological degradation of pesticides in soil is discussed in chapter 3.3.2. (Smith, 1975; Matsunaka et al., 1972; Rosen, 1972; Kearney, Kaufmann, 1975; Rao, 1979).

- Pesticides in the hydrosphere are more commonly found in surface waters than in groundwaters. They are usually dissolved only to a very small extent, as they are mostly adsorbed to suspended substances, especially to organic matter. Pesticides undergo similar chemical decomposition in water as in soil - water being both an environment for reactions, and a reagent (Vročinskij et al., 1979, Ševčenko et al., 1982).

- Pesticides in the biosphere decompose mainly by biochemical reactions. They are primarily subject to oxidation, reduction and hydrolysis affected by enzymes. The resulting substances (intermediates) conjugate via their functional groups with compounds present in the biological environment. They are often still toxic, and in this form enter the soil and water zone again. Pesticide degradability is not the decisive factor in assessing the hazard to water. What is important is whether, due to the degradation of the original substance, non-toxic, equally toxic or more toxic intermediates are created (Klein, 1972).

Findings on the behavior of individual categories of pesticides can be summarized as follows:

a) Nitrophenols and chlorphenols are almost non-persistent substances. They rapidly decompose to non-toxic aminophenols and phenols; chlorphenols are detrimental to senses. When in water, chloracetamides, also, since they are sparingly soluble, rapidly decompose to organic acid and CO_2 (Kearney, Kaufmann, 1975; Ševčenko, 1982; Banker et al., 1980; Matsunaka, 1972).

b) Aliphatic chlorinated acids are not very persistent, do not adsorb to soil, decompose quickly and are readily soluble in water. It is therefore realistic to say that the parent substances are present in ground and surface water and that they migrate over long distances. In soil, water and the biosphere they are degraded by microorganisms, but at higher temperatures. The products of decomposition are not toxic, although they can be odorous. (Foy, 1975).

c) Phenoxy-carbon acids and organophosphates belong among moderately persistent substances; they are adsorbed to varying degrees in clay soils and water sediments. They are decomposed by hydrolysis, oxidation (also photochemical oxidation), reduction, and alkylation/de-alkylation. Non-toxic, toxic and temporarily toxic decomposition products can be created. Among products of decomposition are also substances that damage the organoleptic properties of water. Dioxins, which accompany phenoxy-carbon acids, are toxic (Loos, 1975). This category also includes the carbamates which are degradable in the soil and biosphere by biochemical hydrolysis and the substituted ureas which are degradable by photochemical oxidation and reactions catalyzed by microbes (de-alkylation, alkoxylation). Surface water and groundwater can be less endangered by the above parent substances than the generated intermediates.

d) Bipyridylium herbicides, s-triazines, nitroanilines and organochlorine compounds are relatively strongly adsorbed to soil and are therefore persistent. Differences exist in other aspects. Bipyridylium herbicides decompose rapidly to non-toxic compounds and do not pose a threat to groundwater. S-triazines decompose slowly by hydrolysis, catalyzed by microbes, oxidation, de-alkylation and the destruction of the ring to non-toxic compounds and CO_2 . Hydrolysis is faster when humic material is present. Groundwater can be contaminated immediately after application, for short periods.

Organochlorine compounds slowly decompose chemically by hydrolysis (for example heptachlor, DDT, aldrin, chlordane, dieldrin and endrin). Chemical reactions are catalyzed on the surface of minerals. Photochemical decomposition is faster and gaseous intermediates are discharged to the atmosphere. Biochemical processes are foremost during decomposition, producing non-toxic intermediates (phenols, chlorbenzenes, chlorphenols) as well as toxic intermediates. (Kearney, Kaufmann, 1975; Smith, Myfield, 1978).

Research into the chemistry of pesticidal substances to date has shown that with the exception of categories a and b, these substances, when commonly used, represent to varying degrees a risk to the hydrosphere. Groundwater is generally less frequently contaminated than surface water. Not all effects of the decomposition or persistence of pesticide residuals in the natural environment have been explained satisfactorily yet, especially toxification and detoxification.

3.4.2. Biological degradation of pesticides in soil

Compared to chemical or physical decomposition of pesticides in soil, an additional characterization of pesticides is extremely important in biological studies, that is the effect on the life of microorganisms in the soil ecosystem. The response of the soil microflora to the presence of a pesticide in the environment is important from two viewpoints:

- a) The preservation or change of the complex function of soil as a whole,
- b) The persistence of the pesticide in the soil environment (versus its degradation or leaching).

The highest biological activity takes place in the upper layers of the soil. Thus, the pesticide is most likely to be degraded or immobilized there. When a pesticide is transported to deeper layers, which are relatively abiotic, its appearance in groundwater is more probable. Contaminated water contains active microbes (Cherry et al., 1984), and in many groundwater systems direct microscopic counting proved 10^6 bacteria per gramme of dry sand. Laboratory research has demonstrated that biodegradation of numerous organic compounds, including pesticides, can occur in soil and water. A number of reactions (oxidation, hydrolysis, reduction and dehydration) are catalyzed by enzymes produced in mixed populations of microorganisms. It is very difficult, in fact almost impossible, to forecast the ways and rates of organic compound biotransformation, because the number of species in time and space depends on the environment. Successful research is best achieved by combining laboratory with field experimental studies.

In the context of methods currently available, factors in group a) seems to be measurable with a greater accuracy in field experiments, those in group b) being best measured in laboratory experiments. Factors affecting biodegradation of pesticides in soil are generally discussed below.

Problem of the inoculum: soil contains an unknown number of microbial species, of which only a few are open to contemporary methods of cultivation and identification. After introducing a pesticide into the soil ecosystem the community must adapt, which results in a) suppression of toxic effect of pesticide and b) utilization of pesticides as a regular organic substrate (carbamates). There are two

ecologically important mechanisms for adaptation of a microbial community: a) selection of suitable species and their development (at the community level), and b) induction of enzymes etc. (at the cell level). The above mechanisms of adaptation must also apply when any new intermediates appear in the environment.

Pesticides can be metabolized by microbes either as substrates (i.e. the main source of energy and organic carbon) or co-metabolized with another "natural" degradable substrate. In general, co-metabolism enables the biodegradation of compounds which are otherwise resistant to microbial attack.

Presence of oxygen: some pesticides are reported to be better or only degradable (e.g. DDT) under anaerobic conditions. However, most compounds are better degraded in the presence of oxygen. As the concentration of oxygen in soil is not homogeneous, optimal conditions for the degradation of both various parent compounds and intermediates can theoretically occur simultaneously. In the top layer of soil, where there is the highest supply of oxygen, limitations by water content and also photodegradation can be significant. In deeper layers denitrification, which is a common feature of soil microbes, can substantially extend the range of conditions under which aerobic processes can take place.

Water content: optimal conditions for microbial activity in soil are reported to be about 60 per cent of the full water capacity of soil. The question of the water content affects both the transport of pesticides through the soil and the oxygen concentration; in flooded soils the oxygen is absent.

Adsorption to soil particles: When adsorbed, some compounds are inactivated as well as resistant to microbial attack (paraquat, diquat). As long as the microbes in the soil are also attached to particles, the interaction between the pesticide and the microflora may be more intensive than that estimated from the concentration

calculated per sq. m or kilogramme of soil. In general, longer persistence in soil and suppression of toxic effects by adsorption are factors enhancing the ability of soil microflora to adapt so as to degrade a compound in question.

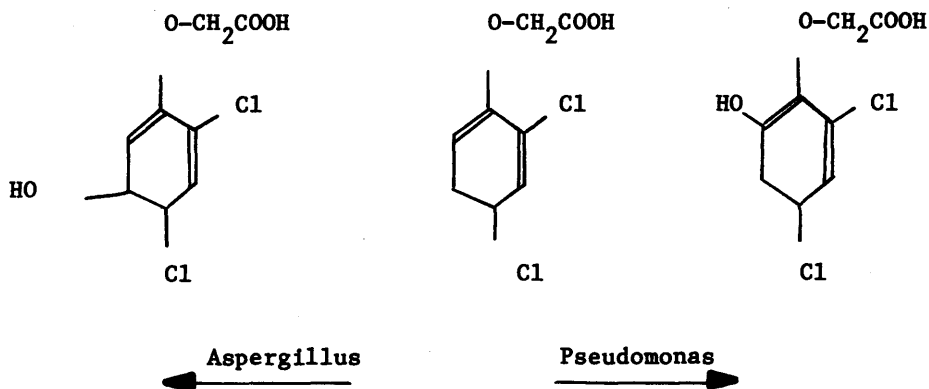
pH value: The adsorption of pesticides to organic matter in soil is generally affected by the pH. In some groups of pesticides lower rates of degradation are reported at lower values of environmental pH.

Organic carbon: organic carbon content is a factor that primarily determines the quality of the soil, microbial biomass and activity, water capacity, adsorption of pesticides etc. All these factors are considered to control the biodegradation capacity of the soil.

In general, factors affecting the interaction between a pesticide and the soil microflora (including biodegradation) can be divided into three groups:

- a) Character of soil (organic carbon, microbial biomass, water content, pH, geological origin etc.),
- b) Character of pesticides (toxicity, resistance to microbial attack, adsorption, solubility, intermediates etc.),
- c) Human or agricultural factors (type of crop, application of organic and mineral fertilizers etc.).

As to the general resistance of groups of pesticides to microbial attack, a special feature of microbial metabolism should be noted. The fate of a pesticide depends not only on its chemical constitution, but also on the microbial species active in its decomposition. For example, 2,4- D is transformed to 5-hydroxy-2,4-D by a soil fungus (*Aspergillus niger*), but to 6-hydroxy-2,4-D by a soil bacterium (*Pseudomonas*):



Thus, as a result of the activity of the complex microbial community in soil, a pesticide can be degraded from more than one site in its molecule, and by more than one metabolic pathway simultaneously. Nevertheless, there are distinct differences in the persistence of various groups of pesticides in soil, a factor which can indicate their relative threat to groundwater quality. The organochloride insecticides are generally the most resistant and can persist in the soil for years. Also certain s-triazines can persist for more than one year. On the other hand, organophosphate insecticides, carbamate and aliphatic acid herbicides show a relatively rapid disappearance, less than 3 months (Hill, 1981; Khan, 1980).

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4. INFLUENCE OF IRRIGATION AND DRAINAGE

E. ROMIJN

4.1. INTRODUCTION

Irrigation and drainage aim at optimizing the net profit from agriculture. The objectives and criteria for irrigation and drainage systems are described in the following sections. A short description is given of different methods of irrigation and drainage. This description makes it possible to understand why adverse effects and side effects sometimes occur. These are illustrated by explanatory notes on case studies, presented during the 16th Congress of IAH in September 1982 and attached to this monograph.

4.2. OBJECTIVES OF IRRIGATION AND DRAINAGE

4.2.1. Objectives

In order to maximize the net profit from agriculture, irrigation and drainage are used to optimize soil water conditions both with respect to quantity (prevention of excess or shortage) and to quality (prevention of accumulation of salts in the rootzone).

Additionally, drainage influences many other tillage conditions, such as:

- structure of the soil,
- traffic movement, prevention of trampling of grassland by livestock,
- aeration of soil which is of importance for rootgrowth and microbial activity e.g. nitrification, nitrogen fixation, decomposition of organic material,
- soil heating. The specific heat of water is 4.19 kJ.kg^{-1} and of

dry soil about 0.8 kJ.kg^{-1} . It follows that for dry soil with a particle density of 2.7 g.cm^{-3} and with $n = 0.5$ the heat capacity is 1.1 J.cm^{-3} and when saturated 3.2 J.cm^{-3} . Soil temperature is of importance for germination e.g. maize requires 16°C , cotton 22°C . Also evaporation of soil water cools the soil,

- root development. Well developed effective rootzones are e.g. for grass and annuals (vegetable crops, potatoes) about 30 - 60 cm; for sugar beet, palmtrees, cotton and citrus about 0.6 - 1.2 m and for maize, grain, sugar cane, alfalfa, rootcrops and orchards about 1.5 - 2 m,
- prevention of increase of salinity caused by capillary rise and evaporation.

4.2.2. Soil water conditions

The waterbalance of the rootzone can be described as

$$I + P + C = E + U_g + \Delta S_w$$

i.e. irrigation I plus precipitation P plus capillary rise C is balanced by evaporation E , groundwater runoff including percolation U_g and change in specific storage ΔS_w .

The saltbalance reads

$$I c(\text{eq})_i + P c(\text{eq})_p + C c(\text{eq})_c = U_g c(\text{eq})_u + \Delta S_w c(\text{eq})_s$$

where $c(\text{eq})$ is the concentration in equivalents per m^3 .

The reason for using equivalents is that they are roughly proportional to the frequently used electrical conductivity EC ;

$$\text{EC} \approx c(\text{eq})/120; \text{EC in } \text{S.m}^{-1} \text{ at } 25^\circ\text{C}.$$

In order to simplify calculations, $Pc(\text{eq})_p$ can be neglected. Furthermore, the following relation holds between the salt content of the

net percolation ($U^* = U_g - C$) and the salt content stored in the rootzone;

$$c(eq)_{u*} = f c(eq)_s + (1 - f) c(eq)_i$$

where f is the leaching efficiency and $(1 - f)$ the ratio of irrigation water passing directly through cracks, fissures etc. For loam, f is about 0.5 and for clay f is about 0.3.

The leaching requirement is the net amount of percolating water U^* , needed to reach a fixed average salt concentration $(eq)_s$ at equilibrium in the rootzone. It can be calculated as follows. At equilibrium, the salt balance is:

$$I \overline{c(eq)}_i = (U^* + E - P) \overline{c(eq)}_i = U^* \overline{c(eq)}_{u*}$$

$$U^* = (E - P) \{ \overline{c(eq)}_i / (\overline{c(eq)}_{u*} - \overline{c(eq)}_i) \} =$$

$$= (E - P) \{ \overline{c(eq)}_i / f(\overline{c(eq)}_s - \overline{c(eq)}_i) \}$$

The irrigation requirement for a fixed average $\overline{c(eq)}_s$ in the rootzone is then:

$$I = (E - P) \{ \overline{c(eq)}_s + ((1 - f)/f) \overline{c(eq)}_i / (\overline{c(eq)}_s - \overline{c(eq)}_i) \}$$

4.2.3. Importance of irrigation and drainage

In the IHP Technical Document of Investigation of the Water Regime of River Basins Affected by Irrigation (ed. Kharchenko & Maddock 1982), the importance of irrigation is illustrated by many figures. In 1970 about 16% of the cultivated area of the world was irrigated, that is 235×10^6 ha, of which 100×10^6 ha were developed in the last 25 years. One third of the irrigated area is situated in China, 27×10^6 ha in India, 20×10^6 ha in the USA and 12×10^6 ha in the USSR. About half of the irrigated lands are situated in arid or semi-arid regions. Particularly in these arid and semi-arid regions, special drainage measures are required because the irrigated lands have

rising groundwater tables and increasing salinity. Kharchenko & Maddock report that in the sixties the damage due to waterlogging and salinity increased in the Indus Plain at a rate of 30.000 ha per year. As a consequence drainage programmes were developed.

In 1975 about 2100 km³ water was used for irrigation; most of it was surface water. However groundwater abstraction is increasing e.g. in the USA 50 km³ per year of groundwater is abstracted for irrigation purposes. Requirements for irrigation are between 5000 - 15000 m³ per year, per ha, depending on the type of crops and the climate. About 100 x 10⁶ ha are protected by drainage systems.

4.3. CRITERIA FOR DEVELOPMENT OF IRRIGATION AND DRAINAGE SYSTEMS

4.3.1. Irrigation

Three principal types of irrigation are identified:

- surface irrigation, either still water flooding (basin irrigation) or flow irrigation,
- sub-irrigation or groundwater infiltration,
- overhead irrigation: e.g. sprinkler irrigation and trickle or drip irrigation.

Surface irrigation is accompanied by surface runoff losses.

Subsurface irrigation supplies crops by way of capillary rise and cannot be used in arid climates because of salinity problems.

Sprinkler and drip irrigation may be highly efficient with respect to losses but may be expensive.

Consumptive water use by crops E is often related to evaporation E_0 of open water by a factor f , $E = fE_0$.

However as the evaporation of open water may be calculated with different formulae or measured with different types of evaporation

pans, it follows that the factors derived by different authors can only be compared if the method of calculation or measurement is known (Doorenbos & Pruitt, 1984). When compared with evaporation of open water calculated by the Penman formula, factors are between 0.8 for short crops and 1.0 for long crops and rice (Romijn, 1985). Examples of seasonal crop evapotranspiration are given in table 4.1.

Table 4.1. Range of seasonal crop evapotranspiration (mm)
(Doorenbos & Pruitt, 1984)

beans	250 - 500 mm	rice	500 - 950 mm
grains	300 - 450	sisal	550 - 800
sorghum	300 - 650	cotton	550 - 950
potatoes	350 - 625	orange	600 - 950
maize	400 - 750	alfalfa	600 - 1500
sugarbeets	450 - 850	bananas	700 - 1700
flax	450 - 900	coffee	800 - 1200
vineyards	450 - 900	dates	900 - 1300
		sugarcane	1000 - 1500

Many crops have sensitive periods during their development. For example cereals are drought sensitive during earing and flowering; cotton at time of flowering and fruit development.

The salt tolerance of crops is judged according to the relative yield of the crop in a saline soil as compared to its yield in nonsaline soil (Richards, 1954). Some examples, relating to decrease in yield of 10 - 25%, are given as limits of conductivity of the saturation extract with distilled water of the soil EC_e (table 4.2.). It should be noted that EC_e is lower than the conductivity of the real soilwater (eq_s) in the range of 20 to 50%.

Table 4.2. EC_e , ($S.m^{-1}$, $25^{\circ}C$) resulting in a yield depression of 10 to 25%

beans, fruit trees	0.2
alfalfa, sugar cane, potatoes, flax, corn	0.4
rice, olive	0.6
wheat, sorghum	0.8
sugarbeet, cotton, date palm, barley, bermuda grass	1.0

During germination many crops are less salt tolerant.

Sodium may cause deterioration of the soil structure, especially in fine textured soils. The soil may become puddled and dispersed thereby causing poor aeration and a decrease in permeability. Nonsaline, sodium type soils (black alkali soils or solonetz) are notorious for poor tillage conditions. Their high pH (8,5 - 10) is toxic and the availability of nutrients like heavy metals is low. The black alkali soils are characterized by the low conductivity of the saturation extract in distilled water, $EC_e < 0.4 S.m^{-1}$ ($25^{\circ}C$) and high exchangeable sodium percentage $ESP > 15$.

Richards (1954) proposed a formula to estimate ESP from the sodium adsorption ration SAR, which can be calculated according to Gapon from the concentration in water in equilibrium with the soil:

$$SAR = [NA^+]/(\sqrt{1/2([Ca^{2+}] + [Mg^{2+}])})$$

$$ESP = \{100(-0.0126 + 0.01475 SAR)\} / \{1 + (-0.0126 + 0.01475 SAR)\}$$

Non saline alkali soils may arise from leaching of saline sodium type soils. Reclamation requires addition of chemicals which reduce the ESP values of alkaline soils, like gypsum, sulphur, sulphuric acid etc. For example, Richards calculates that for replacement of 1 milliequivalent Na per 100 g of dry soil over 15 cm depth of soil profile, a minimum of 1800 kg gypsum ($CaSO_4 \cdot 2H_2O$) is needed per ha.

Initially, considering arid and semi-arid areas, precipitation can be

neglected during the growing season.

The simplified water balance then reads: runoff losses are equal to irrigation less evaporation:

$$U = I - E$$

U comprises conveyance losses U_c and farm or field application losses U_a .

Irrigation efficiencies are defined as follows:

$$\text{conveyance efficiency } e_c = (I - U_c)/I$$

$$\text{field application efficiency } e_a = E / (I - U_c)$$

$$\text{total efficiency } e_p = e_c e_a = E/I$$

Conveyance losses U_c comprise canal seepage which even for lined canals is 5 - 10% of I and operational losses which are due to discrepancies between water supply and demand. Operational losses may be returned to the surface water system.

Farm or field application losses depend very much on the irrigation system used. They comprise percolation losses to groundwater and surface runoff in the case of surface irrigation. Percolation losses can be useful for salt abatement in the soil, but if that is not the case, an extra amount $U^* = \alpha E$ will be needed for leaching requirements. If farm losses are set equal to U^* plus surface runoff, then it follows with surface runoff equal to $\beta (E + \alpha E)$ that:

$$Ie_c = E + \alpha E + \beta (E + \alpha E)$$

$$e_a = 1 / (1 + \alpha)(1 + \beta)$$

For practical reasons $\alpha = 0.5$ will be an upper limit (Drainage principles and applications, 1973). The factor β is 0.2 to 0.3 for basin irrigation and 0.3 to 0.5 for flow irrigation.

Farm or field application efficiencies reported are 60 - 70% for

basin irrigation and 30 - 70% for flow irrigation.

4.3.2. Drainage

The drainage system aims at lowering the water table by reducing drainage resistance to groundwater flow. Groundwater flow may result from precipitation excess in humid climates, irrigation losses in arid climates, or from deep seepage e.g. in valleys or polder areas. The drainage system consists normally of field laterals (ditches or pipes) which are designed to control the groundwater table and collector and main drains to move the drained water. Well drainage is also used.

Many formulae are derived for calculation of drainage systems (Drainage principles and applications, 1973) which will not be repeated here. They are based on a design drainage resistance T which for steady state groundwater flow is equal to:

$T = m/U$, $m = h_m - h_o$ is the difference in height between the water table in the drains h_o and the height midway between the parallel drains h_m ; U is groundwater runoff in $m^3.s^{-1}$ per m^2 of drained area. See figure 4.1.

In case of drainage of infiltrated rainwater or irrigation water in a thin aquifer ($D_h < 1/4 L$) under steady state conditions, the Ernst formula can be used, as follows:

$$T = m/U = m/K_v + L^2/8K_h D_h + (L/\pi K_r) \ln (aD_r/u)$$

U (= groundwater runoff) equals infiltration rate,

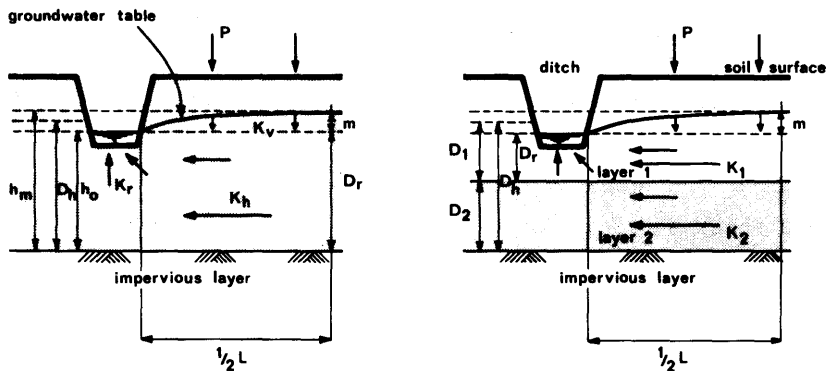
L is drain spacing,

K_v , K_h , K_r are hydraulic conductivities for vertical, horizontal and radial flow respectively,

D_h , D_r are thicknesses of the aquifer and of a layer for radial flow respectively,

a is a geometry factor,

u is the wet perimeter of ditch or drain, $u = \pi r_o$.



$$K_1 \ll K_2$$

$$K_h D_h = K_1 D_1 + K_2 D_2$$

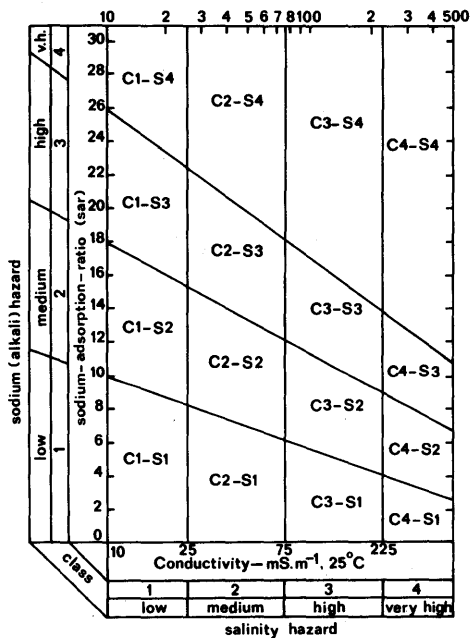


Fig. 4.1. Definition sketch for drainage formulas.

Fig. 4.2. Classification of irrigation water (from USDA Agricultural Handbook 60).

For homogeneous soils $D_r = h_o$, $a = 1$ and for the case in which drains are situated in a clay layer covering an aquifer, D_r is equal to the height of the drain above the base of the clay layer and $a = 4$.

In case of infiltration and/or vertically upward seeping groundwater in a homogeneous thick aquifer:

$$T = m/U = (L/\pi K) \ln (L/\pi r_o)$$

which means that the horizontal flow component disappears.

The water table depth should allow optimal development of the roots of crops, so it should be well below the rootzone, taking into account the full capillary zone.

Under non steady conditions (rain storms, periodic irrigation), the desired water table should not be exceeded on many successive days.

For example, in the Netherlands with a drain depth of 1 m, the design water table depth for grassland is 0.3 - 0.4 m below the ground surface for a net precipitation rate of 7 mm per day, giving

$T = m/U = 85$ to 100 days. In many other countries in western Europe, the designed drainage resistance is of the same order.

Another problem is the required groundwater depth in order to prevent salinization by upward capillary flow. A minimum depth of 1.5 to 2 m is generally required.

4.4. SIDE EFFECTS OF IRRIGATION AND DRAINAGE WITH SPECIAL REFERENCE TO GROUNDWATER QUANTITY AND QUALITY

4.4.1. Side effects of irrigation

In this section the consequences of spraying of waste water from agricultural industries or the disposal of effluents and sewage

sludge from treatment plants are not considered. They are dealt with in the preceding chapters. However, a case study by Goldberg dealing with irrigation of sewage from a cattle pen is attached to the monograph.

Much theoretical work on the influence of infiltrating surface water on groundwater quantity and quality has been carried out in the context of groundwater abstraction following induced recharge or artificial recharge (see e.g. Proceedings Int. Symp. Artificial Groundwater Recharge, Dortmund, 14-18 May 1979, published by DVWK Bulletin 11-14, Hamburg/Berlin 1982). Artificial recharge for water supply purposes is however not considered in this chapter because it is not directly related to agriculture.

The side effects of irrigation depend on climate, source of the irrigation water including quality, the irrigation methods, tillage and fertilizing conditions and also the drainage system. Irrigation and drainage, quantity and quality of the water are all interconnected, however for simplicity they are described separately.

Irrigation, mostly applied in semi-arid or arid areas, implies an irretrievable loss of water from the hydrological system by evaporation, that is the difference between potential evaporation E_p and the evapotranspiration of the crops or vegetation without irrigation. These losses lie between 100 mm in temperate zones and 1500 mm in semi-arid and arid subtropical areas (Kharchenko & Maddock 1982). They impose a heavy demand upon water resources, either surface water or groundwater.

In the case of groundwater abstraction, a drop of the groundwater level of e.g. one meter per year, is no exception. This implies a lowering of 50 m in half a century.

A drop of groundwater level by overpumping may cause harmful side effects such as landsubsidence or with respect to water resources, upconing of underlying saline groundwater or in coastal areas, seawater intrusion.

On the other hand infiltration losses of irrigation water may cause a rise of the groundwater level of the same order. A well known example is the rise of the groundwater level in the irrigated areas of the

Indus Plane of 0.5 to 1 m per year or 30 to 40 m since the beginning of the century.

The paper by Agarwal et al. provides a very good example of the problem of changes in groundwater level and the salinization problems in semi-arid areas with shallow groundwater in the Haryana State (NW India) under irrigation.

Two main side effects of irrigation with respect to groundwater quality are: leaching of salts accumulated in the soil and leaching of fertilizers. In arid and semi-arid regions the salinity of the soil saturation extract may rise to 2 to 10 times the concentration of the irrigation water (Richards, 1954). If irrigation takes place with surface water with an EC of 0.1 to 0.2 S.m^{-1} (or mhos per meter) which is equivalent to a salt concentration of about 1 g/l, the soil saturation extract reaches a concentration of 2 to 20 g/l. Irrigation with water of 0.1 to 0.2 S.m^{-1} is a common practice in large parts of the world (Fig. 4.2.).

In order to maintain agriculture, even tolerant crops like barley need leaching requirements of about 20% of the irrigated water. This means that the groundwater will have a salt content of several g/l which makes it unsuitable for many uses including agriculture and drinking water.

Leaching of fertilizers results from irrigation losses or return flows. The paper by Burden explains that irrigation of lowland plains in New Zealand has intensified livestock farming, resulting in more urine production from grazing sheep together with leaching of about 25% of excreted nitrogen. Nitrate concentrations in the alluvial aquifers have surpassed the critical value of 50 mg/l.

4.4.2. Side effects of drainage

The side effects of drainage depend on the texture and chemical composition of the soil. Secondary side effects result from intensification of agriculture, related to drainage. Intensification results

in a higher use of fertilizers or higher density of livestock and related hazards for groundwater pollution. Besides intensification of agriculture, drainage may cause acidification of soils containing sulphides and combustion of peat layers, both by aeration.

Drainage may have positive or negative effects on groundwater replenishment. A lowering of the groundwater table results mostly in a higher infiltration rate of precipitation and a lower evaporation rate. On the other hand, drainage causes a higher groundwater runoff which may prevent deep percolation and groundwater replenishment.

Some special cases will be mentioned here relating to reclamation of soils. Reclamation of peat soils by drainage results first of all in landsubside. Landsubside is caused by consolidation of the layers below the groundwater level and by oxidation and shrinkage above the groundwater level. Measurements in the peat area in the western part of the Netherlands showed that a lowering of the water level in the ditches from about 0.3 m to 1.0 m below landsurface resulted in a subsidence of 10 cm in 6 years; 4 cm due to consolidation, 1.5 cm due to shrinkage and 4.5 cm due to oxidation. During the last 900 years, landsubside amounted 2 m under conditions of shallow groundwater tables, of which 85% was due to oxidation, that is about 2 mm per year. For water quality, it is of importance that oxidation of peat gave a yearly production of $160 \text{ kg N} \cdot \text{ha}^{-1}$ with ditch water levels of 0.3 m and of $480 \text{ kg N} \cdot \text{ha}^{-1}$ at levels of 1.0 m. Half of the nitrogen produced was taken up by grass, and half was leached to the groundwater. With an infiltrating precipitation excess of 200 mm per year, a loss of 80 kg nitrogen gives a concentration in groundwater of 40 mg N per liter whilst a loss of 240 kg gives a concentration of 120 mg N per liter, both concentrations far above the drinking water limit of 11 mg N/l. In total, at a ditch water level of 0.3 m, $4000 \text{ kg} \cdot \text{ha}^{-1}$ organic dry matter is lost annually by oxidation and at a level of 1.0 m, $12000 \text{ kg} \cdot \text{ha}^{-1}$ (Schothorst, 1977). In subtropical areas e.g. Everglades in Florida, oxidation of peat may result in a loss of about 5 cm per year.

Reclamation of soils rich in sulphides (FeS , FeS_2) may cause water quality problems. These soils are formed in inundated coastal areas or in lakes. Aeration during reclamation and drainage causes oxidation of sulphides to sulphates. The sulphate content in heavy clays may amount to 1 to 10 g per 100 g dry soil matter (Drainage principles and applications, 1973). In the case of non-calcareous soils, ferric and aluminum sulphates are formed, and the pH of the soil may drop to 1 or 2. In the Netherlands, these soils are called "cat-clays". In the Wieringermeerpolder in the Netherlands, in the first year after drainage, 150 tons per ha CaCO_3 were needed to neutralize the arable layer. The leached sulphates will make the groundwater unsuitable for many purposes. Reclamation and drainage of polders in coastal areas may cause a seepage flow from the sea to the polders, causing salinization of the groundwater by seawater encroachment. Some case studies are available in the proceedings of the International Symposium Polders of the World (1982).

List of symbols

TERM	SYMBOL	UNIT
molar concentration of A	$c_A, [A]$	mol. m^{-3}
concentration of A	$C_a, [A]$	g.m^{-3}
capillary rise (cumulative)	C	mm
field application efficiency	e_a	--
conveyance efficiency	e_c	--
total efficiency	e_p	--
thickness of aquifer	D	m
cumulative evaporation	E	mm
electrical conductivity	EC	S.m^{-1}
crop factor	f	--
leaching efficiency	f	--
hydraulic head	h	m
irrigation depth	I	mm
hydraulic conductivity	K	m.s^{-1}
drain spacing	L	m
head difference in drainage system	m	m
precipitation depth	P	mm
specific storage	S_w	mm
wet perimeter	u	m
runoff depth	U	mm
field application loss	U_a	mm
conveyance loss	U_c	mm
specific groundwater discharge	U_g	mm
net percolation	U^*	mm
drainage resistance	T	s

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5. MATHEMATICAL MODELS

J. BALEK

5.1. SYSTEM APPROACH

Mathematical modelling in groundwater quality management covers a broad range of techniques, from the application of algorithmized simple analytical formulae to advanced numerical schemes. Each of the models has its place in groundwater quality management, and at present there is a model available for the solution of any groundwater quality problem. Selection of the model adequate to a given problem depends on several factors. Time available and economical budget may become decisive factors in many types of studies. However, technical aspects such as the amount and quality of data available, the degree to which the simulated system can be identified, and analysis of possible constraints, are most significant factors.

Selection of the proper type of the model for a given problem, considering the many models described in the literature, is not an easy task either. The great complexity of problems related to crop production on one side and water quality on the other, various practices of fertilization, impact on the environment etc., are often found as very specific to a given problem. Thus, instead of attempting to select a proper model, the potential user may make the decision to set up a new one. However, development of a new model is time consuming; it is often more convenient to select a model already accomplished and tested.

Such a selection should be based on a solid system-approach solution; for instance, as has been applied in the selection of specialized hydrologic and water resource models by Buras (1972). This approach consists of

- identification of problem to be solved,
- identification of available data,
- identification of the simulated system,
- identification of constraints,

- selection of the model,
- testing of the model,
- adaptation of the model.

5.1.1. Identification of the problem

This part of the work should be accomplished jointly by the user of the results and by the person or team responsible for the solution. The user represented by the organization or institution, is often unaware what type of results can be achieved by the model; which constraints can be expected, and that there are many problems which can be solved more simply without any model application.

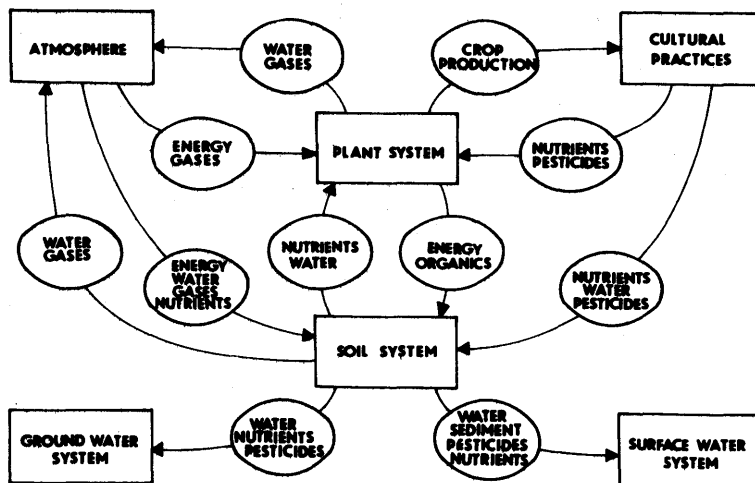


Fig. 5.1. Lyons' graph of possible interactions between crop production and the other parts of the environment.

Figure 5.1. is Lyons' graph (1980), of all possible interaction between crop production and the other parts of the environment. The graph indicates the complexity of possible problems. If, for instance, groundwater quality should be simulated, other parts of the environment, such as the surface water system, plant system, soil system, agricultural practices and atmospheric conditions must not be neglected. Thus, many other processes enter into the simulation even if not specified in a preliminary request.

5.1.2. Identification of available data

As soon as the problem likely to be solved has been specified, it is necessary to find out the quantity and quality of data which can be collected in the region as an initial source of information and as model input. With some models there can be special requests for data which are not commonly available outside of the model catchments or pilot schemes.

Identification should be concerned with basic data first; then the special data are reviewed. The quality of data should be checked very carefully, together with the reliability of the source. Also, the length of the periods of data availability has to be determined, and gaps in the records identified. Availability of the data in the future and possible extension of the network should be examined.

A review of data most frequently required as an input into water quality models is in table 5.1.

5.1.3. Identification of simulated system

The identification is based on the field survey and on the analysis of maps indicating the topography, soil types, vegetation, geology and other features. Also, hydrogeologic maps showing extent and boundaries of all aquifers and aquicludes, transmissivity maps and

Table 5.1. Inputs required for water quality models.

TYPE OF DATA	SPECIFICATION	AVAILABILITY
Climatology	rainfall, temperature, wind velocity, air moisture, radiation, sunshine,	fair with the exception of rainfall rate, good, less frequent, fair, poor, fair,
Hydrology/erosional processes	hydrograph components, more than 20 parameters characterize erosion in advanced models, properties of the aquifers,	fair in daily values, Some available from map, another have to be estimated or obtained from field/lab.experiments.
Soil	porosity, profile, structure, soil water limits, infiltration, soil freezing process,	basic information available from maps, handbooks etc, field survey depends on time and budget available.
Vegetation	type, leaf area, root depth, seasonal development,	same as for soil.
Chemistry	type of pollutants, amount stored, amount inserted, time of application, chemical properties of pollutants, geochemical properties of the aquifer,	fair.

maps showing variations in storage coefficient and hydraulic connection of streams to aquifers are useful. Additionally, information on the type and location of recharge areas, surface water diversions, groundwater pumpage, areal distribution of water quality and potential sources of pollution should be identified.

All reports, documents and papers relevant to the region should be examined.

5.1.4. Identification of constraints

Besides considering time limits and the available budget for the modelling, the capacity of the available computer and the possibility of forming a team of specialists, who may be needed for more advanced solution, should be considered. Also, local legal and administrative rules can be found to be limiting factors.

5.1.5. Selection of the model

This step is the result of the previous identification. A quick orientation with the many existent models is a difficult job, even for experienced users, because of the vast number of water quality models that have been described in the literature, the quality of which cannot be compared without direct application. However, as stated by Prickett (1980): "...despite the impressive array of mathematical models and computation devices there are definite areas of needed improvements which include making present and future models useful by adequately documenting codes and procedures for application; developing a large group of models aimed at solving problems in the range of simple to moderate complexity, and developing models and techniques that produce results managers can understand".

Pioneering work has been accomplished at the Institute for Applied system Analysis at Laxenburg, Austria, where the most renowned models have been collected, implemented and tested. Experienced advice can

be obtained there. Also, a Clearing House for Groundwater Models has been established at the Holcomb Research Institute, Butler University, Indianapolis, Indiana, USA, which compiles, catalogues and disseminates information on available models developed in governmental and private sectors.

However, it may still happen that the users run into the problem of obtaining someone else's model and then being unable to use it because the manual did not adequately explain how to apply the model both from operational and credibility standpoints.

Under certain circumstances when system cannot be adequately identified and for some cases, the model application may have to be rejected.

5.1.6. Testing of the model

Often it has been found to be convenient to test the model in an index (reference) area in the studied region, for which highly accurate data have been prepared. The model can be calibrated there and then its validity extended. Some authors claim that their model does not need any calibration, which sooner or later is found not to be correct. Also, the credibility of the manual has to be verified, considering the computer system available.

5.1.7. Adaptation of the model

Providing that the model has been found to be suitable for the problems to be solved, the model may require further adaptation for practical application. Typically, this work consists of the reorganization of the data bank, adaptation of the headings, redistribution of the outputs in a more readable form and changes of the units used. This work should be done carefully to avoid any damage to the model structure.

5.2. CLASSIFICATION OF THE MODELS

There are several ways for classifying the models concerned with various aspects of water pollution. The wide field of problems and levels at which the models are solved indicate many possible approaches toward classification.

Form the applied point of view there are three types of classification which can serve as guides as to when a a specific problem is to be simulated at a certain level for a given purpose. To all models available of a specified type is beyond the scope of this paper. Therefore, only a few models are given as examples. Such models have been selected which provide a wide list of references, so that the potential user can find additional information about specific models.

5.2.1. Classification considering the process modelled

Chemical and sediment loading models

In this group belong the chemical transport models which estimate effects of transported chemicals on water quality. These models simulate the response of the regional water resources to both point and non-point sources of pollution. The sediment transport models are included in this groups as well. The sediment itself is not a serious water quality problem, however, it often contains various types of chemicals washed out of the drainage area to the river network. Thus, erosional sediment loading models frequently are a part of chemical transport models.

In general, these models simulate the transport of airborne pollution in rain, falling in the form of aerosols or coming from another sources. From the hydrological point of view, surface runoff, inter-flow and groundwater flow, together with rainfall distribution, are significant.

Also, unsaturated water flow and capillary zone flow is important. While the interflow and groundwater flow can transport dissolved chemicals, surface runoff carries both dissolved and solid-phase chemicals, the latter ones being transported with the sediment. Transport models usually describe the chemical losses from the land surface and/or from the root zone by means of several water balance components.

Haith (1980), listed nineteen principal models of the above described type. In the same publication information on each of these models can be found.

Water quality impact models

These models have been thoroughly analyzed by Zwirnmann (1981). They are designed for the simulation of the response of a water body to any kind of pollution. Thus, they are concerned with both point and non-point sources of pollution. These models are used, for example, to identify the chemical leaching potential of soils, risks from chemical pollution in various regions and subregions, nitrate concentration changes under various agricultural practices, including long-term agricultural development strategies. Also, they consider various management alternatives from the viewpoint of pollution control. In some of these models water quality under various types of water resources exploitation can be examined in an attempt to determine the most suitable water management practices.

Young et al. (1976), using the modelling approach analyzed the effect of groundwater exploitation from chalk in Hampshire, England, on the water quality and the interaction between the agricultural practices and quality of groundwater pumped.

An integrated approach toward the simulation of the land use impact can be found in the model of Dudek and Horner (1981), simulating an

integrated physical-economic system of irrigated agriculture. Zwirnmann (1981), also examined six models of this type.

Agricultural planning, economic and management models

These models describe the economic implication of alternative management practices with the aim to control agricultural non-point sources. The use of some of them also favors the analysis and optimization of environmental and production objectives. Most of these models are based on a budgeting approach which quantifies resources requirements, financial benefits and costs relevant to the agricultural management practices. The transfer of financial aspect of simulation from country to country can be found to be difficult considering different economic approach to simulated problems. The relationships and formulas can, however, serve as modelling guides rather than for the immediate application.

Regional impact model provide marco-scale evaluation of agricultural management on crop distributions and other economic measures. Watershed planning models are developed for specific water quality problems such as the control of agricultural practices in the relation to eutrophication, sedimentation, etc. Farm management models evaluate the impact of pollution sources on income and management practices of individual farmers. Nineteen models of this type have been evaluated by Haith (1980), comprising a wide scope of simulated problems.

In figure 5.2. an example of the simulation of integrated land use, water resources and water quality and their relationship to the economics for the San Joaquin California, USA, by Horner and Dudek (1979), is shown. Obviously the boundaries between the second and third group of models are not very rigid and some of the models can be considered as pertinent to both types.

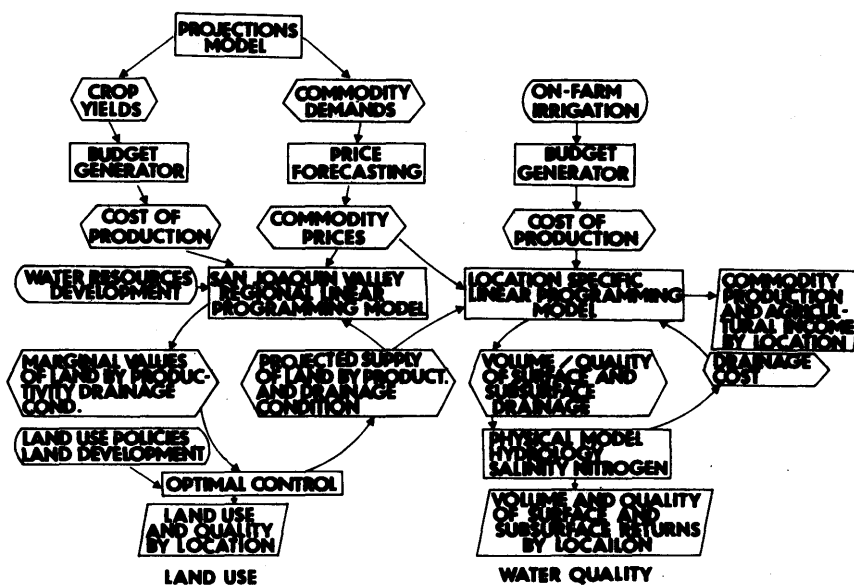


Fig. 5.2. The simulation of integrated land use, water resources and water quality by Horner and Dudek.

5.2.2. Classification considering mathematical approach

Black box models

To this group belong the models which solve the relationship between given input and output when the physical background of the process is not fully known. The transient function originates mainly from practical experience with the behavior of simulated variables.

Greenwood and Burns (1979), examined mathematically more complex models available for water quality analysis and concluded that "...flow theory models require detailed data that is unlikely to be widely available and that contrary to many tacitly held beliefs, models developed from the flow theory approach are not based on any more fundamental principles than less complicated ones".

Another reason for simple black box modelling is the low cost of computer time.

As an example the model of Burns (1980), was based on a simplified assumption of nitrate flux through horizontally stratified soil layers. Burns' nitrogen calculator distributed to British farmers for predicting nitrogen losses by leaching during winter and spring, calculates the nitrogen leached from the rainfall data, soil type, critical rooting depths and weekly evapotranspiration values.

Conceptual models

These models describe physical processes in the watershed/field by empirical formulas which are supported by field and laboratory experiments. Each significant physical, chemical and biological process which takes place within a system is mathematically defined with the description reflecting present verified understanding of the described part. Sometimes two subtypes of models are recognized: empirical, with formulae derived empirically, and deterministic, using mathematically more reasonable laws of hydrodynamics, chemistry and biology. However, as stated by Lyons (1980), "...what we define as scientific law today can be seen as simplified interpretation tomorrow".

Lyons found following basic principles in the conceptual models:

- a) Compartment analysis, used for instance by Atkins (1969), in multicompartment models for biological systems, and by Patten (1971), for ecological simulation.
- b) System dynamics as applied by Forrester (1961).

- c) Energy circuit language as used by Odum and Odum (1976), in energetic simulation.
- d) Discrete physico-chemical approach as described by Smerage (1979), in physiological modelling.

The approach can be analytical when watershed behavior is analyzed initially as a complex and step-by-step broken down into water quality balance units, and synthetical when partial models are compounded into the final solution.

The CREAMS model (Knissel, 1980), is an example of the above. More than 40 specialists cooperated during the preparatory stage with the purpose being to set up a synthetic conceptual model. During the preparatory stage a physically-based model with a limited number of parameters was derived. Nevertheless, more than 100 parameters were found to be significant in the final version. Additionally, monthly temperature and radiation data were desired together with daily rainfall. Partial submodels describe hydrological processes, erosional processes and the flux of dissolved and adsorbed plant nutrients and pesticides. The hydrological model is superior, providing data for both erosional and chemical model. Results of erosional simulation serve as an input into the chemical model. A system approach as given in figure 5.3. indicates the deterministic solution.

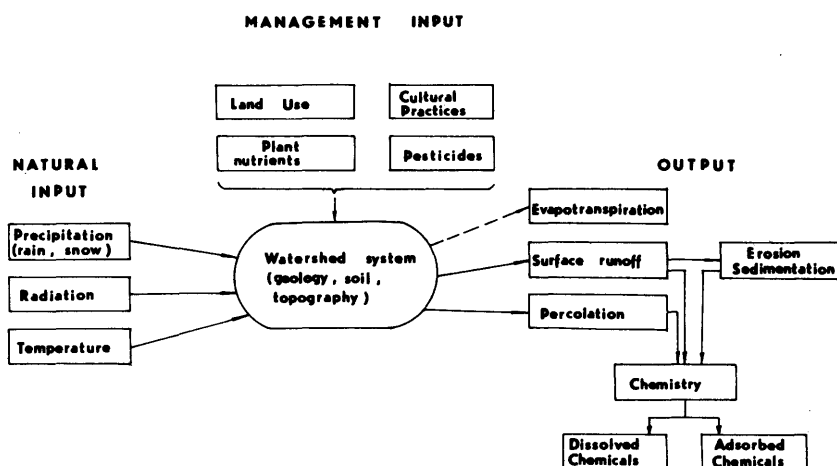


Fig. 5.3. Deterministic approach in the CREAMS model, after Knissel.

Sometimes it may be found to be difficult to obtain all data and parameters desired at the same confidence level. Possible errors which may result from such inadequate inputs need to be examined before actual application (Balek, Palouš, 1982).

Statistical and stochastic models

In contrast to the conceptual models, these models consider the chance of occurrence of simulated events. Thus the concept of probability is introduced into the simulation. A statistical model of a geophysical process introduces probability concepts into the simulation. A stochastic model of geophysical processes also takes time factor into account.

Providing that certain laws of probability are valid for the whole sequence, the time series is considered to be stationary, in contrast to the nonstationary time series the variables of which are mutually independent.

Both types of models are applied when the physical background of the simulated process is not known, no matter for how long observation records are available.

In water quality simulation these models have not been widely applied. Vályi (1980), provided an example for the statistical evaluation for the determination of the maximum level of crop production for the year 2000, as a result of optimised utilization of the natural resources.

Balek and Kalábová (1981), applied models of hidden periodicities, the coherence model, the model of the demodulation and the multidimensional Markov model when analyzing possible impact of man's activity on the hydrological regime of springs of Karlovy Vary. Considering the complexity of the processes involved, any other model approach was not found to be suitable. Figure 5.4. is given as an

example of the multidimensional Markov simulation of the flow discharge regime dependent on the sulphate and chloride content and on the total dissolved solids content.

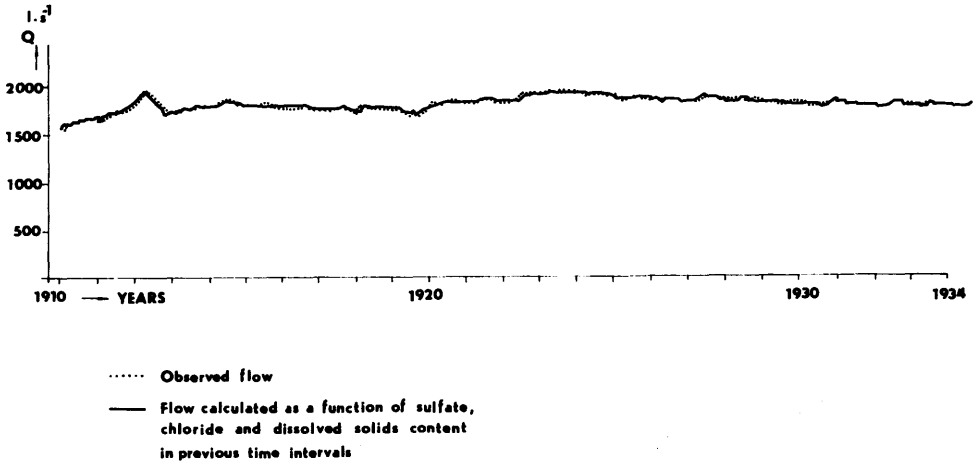


Fig. 5.4. Multidimensional Markov simulation of the flow regime dependent on the sulphate and chloride content, and on the total dissolved solids content. After Balek, Kalábová.

Dynamic models

Van Veen and Frissel (1980), stated that dynamic models are based on the description of the system by differential equations. The processes considered are similar to those as solved by previous types of models, but usually are described more in detail. The differential equations are sometimes numerically integrated. The models are divided into two types: these using explicit methods and those using implicit methods.

James (1976), divided dynamic models into two categories: optimization models using linear and dynamic programming techniques and dispersion models simulating the movement and dilution of pollutants in situations of great hydraulic complexity. To the second group also belong finite difference and finite element models which are based upon the general mass balance equation for salinity, Alabaster (1973).

The model of Beck and Frissel is given as an example. Beside describing physical and chemical processes such as volatilization of ammonia, leaching and fixation of ammonium on clay minerals and diffusion of NO_3^- and oxygen, it describes also microbial processes, nitrification, denitrification, mineralization and immobilization. Growth of the heterotrophic biomass is considered to be dependent on the availability of carbon and nitrogen-compounds. The processes are described at a high mathematical level.

In the same category belong the models of Simmons et al (1978), and Tanji et al (1980), simulating the same the processes. The model of Wagenet (1980), also simulates heat flux. Kruh and Segall (1980), developed a model in which an emphasis is on nitrogen as relevant to water movement.

A difficult problem in simulating the nitrogen flux in unsaturated soil was solved by Cameron and Kowalenko (1976). Microbial activity in relation to mineralization and immobilization was simulated by Juma and Paul (1980). The transport of C, N, P, K at one time was simulated by Smith (1979).

The present trend is directed toward the highly specialized models describing various processes of water quality in detail. For instance, some models deal with the various phases of the soil-nitrogen cycle. Even within such a group there exist even more specialized models concerned with the kinetics of the NO_3^- reduction process only. Denitrification is solved by first order kinetics, zero order kinetics or so called Michaels-Menten kinetics.

As can be seen in figure 5.5., which is a flow diagram showing the relationships in the mineralization-immobilization process, Van Veen and Frissel (1980), the simplified flow charts of conceptual and dynamic models are very similar and the difference is found only in the more advanced theoretical approach.

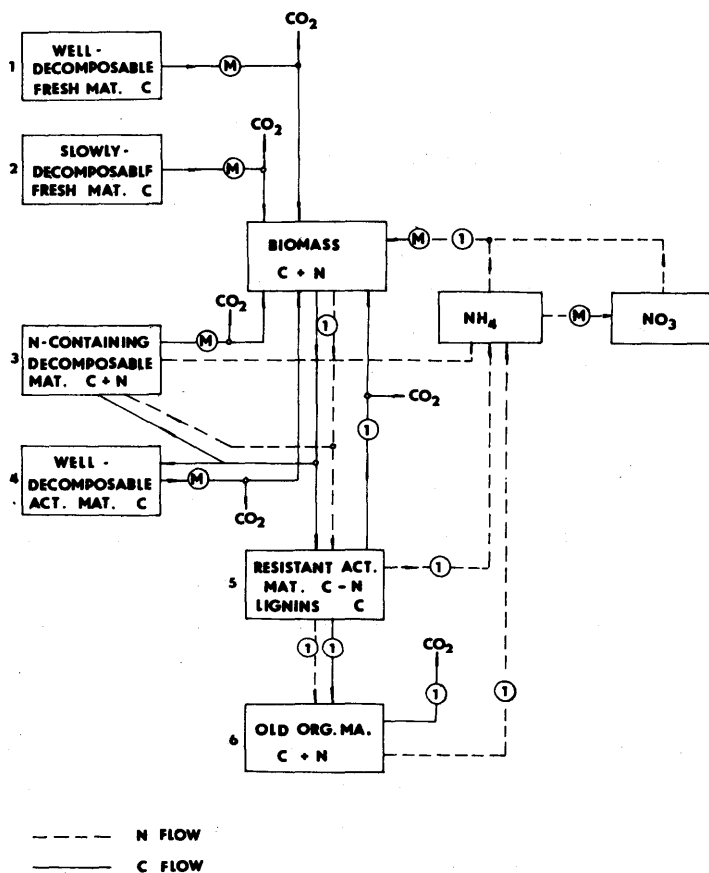


Fig. 5.5. A flow diagram showing the relationships in the mineralisation-immobilisation process, after Van Veen and Frissel.

5.2.3. Classification considering the purpose of the models

Three types of models can be recognized in this group: models for better scientific understanding; models for managerial application, and forecasting models (Shvytov, Vasiliev, 1980). Such a classification can be considered as more less arbitrary because some of the models can cover more than one task.

Scientific models

Scientific models are very important in basic research, being considered as effective tools for the promotion of a deeper knowledge of complex systems and/or specific problems within a general system. Often, however, the amount of data required as inputs can be obtained only from a limited number of well instrumented experimental areas or only from laboratory experiments. With increased quality of data and advanced water quality monitoring, some of the scientific models can be adapted later for managerial purpose or for forecasting.

A comparison of results achieved by various scientific models contributes also to a further development of the theory. In general, any model which has been based on exact biological, chemical and physical descriptions of the process mechanisms involved, this going beyond present knowledge, can be considered as scientifically oriented, even if its immediate application in practice is not possible. It should be mentioned that the scientific models are not necessarily oriented only to the dynamic models as described in previous classification. Any mathematical tool can be found to be sufficient at a certain stage of basic research.

Model approach addressing the retention, transformation and transport of pesticides in soil-water systems as developed by Rao and Jessup, 1980, can be given as an example. As stated by the authors "...from the large number of field studies conducted on pesticide persistence only a limited amount of data could be used for model verification... The very accuracy with which laboratory measurements can be made and our mathematical ability to devise complex simulation models seems to be diverting our attention from the development and testing of simple models for field application". The theoretical background of both authors and their experience in the theory of pesticide transport entitles them to such a conclusion.

Managerial models

Actually most of the models developed should be sooner or later utilized for the solution of practical problems. The application of many models for such a purpose requires the adaptation of previously scientific models. Particularly, the manuals need to be modified into a form which is understandable to a potential user. The parameters and data serving as inputs should be clearly defined and the outputs should be arranged into a form which can be immediately used.

Moving up from local to regional water quality systems one tends to find it economically feasible to use models more extensively. Therefore it has been found to be useful to organize the models into groups aimed at solving problems of simple to moderate complexity. At IIASA an approach has been followed which groups specialized types of models into groups. Each model is described more or less in the same way which facilitates the selection of an adequate model.

As an example we can consider the list of cropland phosphorus transformation and loss models by Shvytov (1979), in which the state-of-the-art for that field is evaluated. An example of the model description of one of the models, described in the cited work, given in table 5.2., is self-explanatory. There are another ways of model description which may also include information on computer facilities and language required, operational costs, references etc.

Forecasting models

The models capable of forecasting can be divided into two groups. One type of model provides the forecast on a long-term basis or in a regional to global scale; another type provides real-time forecasting in short time intervals. Both types of models can work at the managerial and scientific level as well, and any type of mathematical approach can be followed.

Table 5.2. An example of model description

Model reference	L.J. Tubbs; D.A. Haith, "Simulation of nutrient losses from cropland," Paper No. 77-2502 was presented at the 1977 Winter Meeting of the American Society of Agricultural engineers, Chicago, Illinois, December 13-16, 1977, 34 pp.
Modelling processes	Water balance processes: surface and subsurface runoff, snow-melting, percolation, evapotranspiration. Nitrogen balance processes: organic nitrogen mineralization, runoff and percolation losses of nitrogen, crop uptake of nitrogen. Phosphorus balance processes: absorption and desorption of inorganic phosphorus in the soil, soluble phosphorus losses in runoff, adsorbed losses of phosphorus with erosion.
Modelling techniques	The hydrological submodel is based on a daily moisture balance for the top layer of soil. Runoff is forecast using the U.S. Soil conservation Service's equation. The organic nitrogen mineralization rate is modelled by the Van 't Hoff-Arrhenius relationship. The equilibrium between fixed and soluble phosphorus is described by a linear isotherm. Average soil losses due to erosion are calculated from the Universal Soil Loss equation.
Model input	Daily weather data (surface air temperature, solar radiation, total precipitation, minimum and maximum daily air temperature), nutrient inputs and crop removals are considered as a main model input.
Model output	Losses of nitrogen and phosphorus in eroded soil, losses of dissolved inorganic phosphorus in runoff, losses of dissolved inorganic nitrogen in runoff and percolation are the main output of the model
Model assessment	This model can be used to predict losses of fertilizer and nitrogen from an agricultural cropped field. The present model does not provide for the assessment of the effects of changes in manure applications. It should be noted that unlike other existing nutrient simulation models, this model provides reasonable estimates of phosphorus and nitrogen losses.

For real-time forecasting any type of model can be used for which the data input from standard network can be provided in preselected time intervals and which can be applied for a direct simulation of the impacts. Real-time system is at present available on most of the standard computers.

Long-term forecasting is usually based on hypothetical data, which can be expected for the future in optimistic, normal and pessimistic variables. Oakes (1981), provides an example of the prediction of nitrate concentration in pumped water in Kent (Fig. 5.6.). The model has been run from the year 1800 to 2100. Early data are of low reliability and the present level of fertilization is expected to be maintained in the future. A similar approach was reported by Mallick and Lal (1982), for the Indo-Ganga Plain, India.

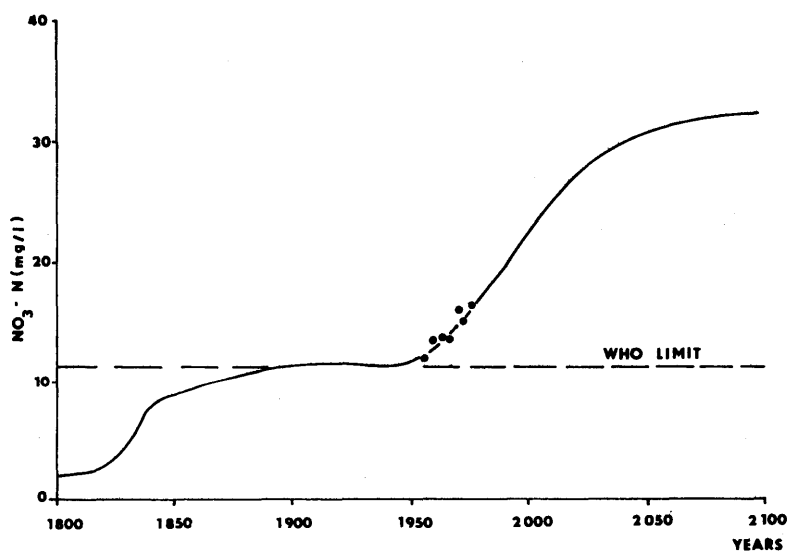


Fig. 5.6. Oakes' prediction model of nitrate concentration in Kent.

Many more types of models can be utilized for such a purpose. Golubev (1980), defined the world landscape zones where the future hazards of nitrate leaching can be expected to be high, such as coniferous forests, dry steppes, semi-deserts and areas of temperate climate.

5.3. CONCLUSION

The state of the art of mathematical modelling is well advanced with a large number of models available for a wide variety of simple to very complex water pollution problems. Computational devices offer a wide variety of means for solving mathematical models everywhere.

Needed progress in simulation includes development of models in the areas of solving problems of simple to moderate complexity; making models more useful by improving their documentation, particularly manuals and software and producing materials which make modelling more utilizable by the decision makers.

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6. GROUNDWATER QUALITY MONITORING UNDER DIFFERENT AGRICULTURAL CONDITIONS

J. VRBA

6.1. INTRODUCTION

Groundwater quality monitoring systems play an important part in the protection of hydrogeological systems. The design and operational management of such systems at the national, regional or local level, the unification and optimization of sampling methods and monitoring frequencies, data acquisition, transmission, processing, storage, retrieval and analysis, the legislative and technical implementation of protective measures, and determination of control measures are the principal components of a monitoring system.

In a number of countries national or regional groundwater quality monitoring systems are already in operation, covering selected wells, springs, streams, rainfall stations, domestic, local or regional water supplies, and existing and potential pollution sources.

Groundwater as part of the total hydrological system is rarely contaminated sooner than surface water. The response of aquifer systems to anthropogenic impact is not immediate, but delayed. This delay time is important from the point of view of groundwater protection.

If a monitoring system already exists, the contaminant can be identified and its movement recognized while still in the unsaturated zone, rehabilitation and remedial measures can be started immediately, and aquifer contamination can be prevented. If the contaminant is detected in the saturated zone, monitoring makes it possible to accelerate its isolation and the choice of a cleanup process or a removal technique. The time and space effects of the contaminant on the groundwater system are thus substantially limited.

When no monitoring systems exist our ability to protect groundwater is much reduced. Groundwater contamination is usually sudden and without warning.

Removal of a pollutant from a groundwater system is complex, long-term and financially demanding. Pollution affects not only the hydrosphere but also has economic, social and ecological consequences that are always much more serious and considerably costlier than the design and operation of a groundwater quality monitoring system.

Groundwater quality monitoring is a complex process requiring the establishment of long-term or short-term monitoring programs. The purposes and objectives of monitoring are to determine physical, chemical and biological properties of groundwater, identify time and space effects of natural processes and human activities on the hydrogeological system, forecast changes in the water quality, and define measures to be adopted for groundwater prophylactic protection and those for the restoration of groundwater which has already been polluted.

6.2. SOURCES OF POLLUTION PRODUCED BY AGRICULTURAL ACTIVITIES

The integrated impact of different pollution sources must be taken into consideration when a groundwater quality monitoring system is being established in an agricultural region. Agricultural activities frequently have many impacts on the soil-water system. (through fertilizing, irrigation, pesticide application, etc.).

The main agricultural sources of groundwater pollution are animal wastes, fertilizers and soil additives, pesticides, and irrigation return flow.

6.2.1. Animal wastes

Animal wastes are classified as solid and liquid (see Chapter 3). Farms specializing in beef or milk production where thousands of animals are concentrated in feedlots or dairies produce about half a tonne of manure on a dry weight basis per animal in the feed period (120 to 150 days) - Everett (1983). The quantity of manure greatly exceeds the needs of the farm land.

In these regions manure and animal wastes are applied to arable or grass land in amounts much exceeding the retention capacity of soil and the needs of plants.

It is not exceptional to find livestock farming areas where some 300 to 600 kg of phosphate (P_2O_5) is applied per hectare/year. Fertilizing with animal wastes (manure, slurry) may become a source of non-point groundwater pollution. Silage liquors and uncontrolled spillages of liquid wastes from manure stockpiles into groundwater produce point pollution.

In such areas monitoring systems should focus on nitrogen compounds (ammonia, nitrates, nitrites), pH, conductivity, BOD, chlorides and phosphorus compounds. In the case of a shallow aquifer, with a thin unsaturated zone and very permeable soil, monitoring should also cover bacteriological pollutants, particularly faecal coliforms and streptococci, and pathogenic microorganisms.

6.2.2. Inorganic fertilizers and soil additives

Inorganic fertilizers are, especially in Europe, a frequent source of groundwater non-point pollution. pH, conductivity, nitrates and/or phosphate, ammonia, potassium, calcium, chlorides, fluorides and sulphates in groundwater should be monitored, above all beneath arable lands under intensive agricultural activity. Phosphate fertilizers may contain heavy metal pollutants, and therefore cadmium, chromium, copper etc. should be monitored also. Tritium and/or ^{14}C analysis is desirable to determine the age of water and the transport processes. In the soil layer, the monitoring of pH and the C : N ratio, as well as the seasonal changes in the soil organic matter are considered to be important in view of the physical and biochemical processes in the unsaturated zone. Monitoring activity in regions with arable land should also include the unsaturated zone, particularly in areas with sandy soils and vulnerable aquifers, and in recharge areas of public water supplies.

If lime and gypsum are applied, the soil's physical properties and the pH of soil and groundwater should be monitored, as well as the TDS (Total Dissolved Solids).

6.2.3. Pesticides

When normal doses of pesticides are applied they will only reach groundwater in undesirable concentrations under quite exceptional conditions. Groundwater pollution by pesticides is therefore rare. Uncontrolled handling of pesticides during storage, or accidental spills during transportation may cause local pollution of groundwater. In such cases it is recommended that a special monitoring system be designed which will continue working even after the rehabilitation processes in the hydrogeological system have been completed. Pesticide contents in groundwater supply systems with recharge areas covered by arable lands should be monitored regularly, as even minimal concentrations in potable water are unacceptable. Well-equipped laboratories, with mass spectrometers, should be available for pesticide analysis. Organochlorine and organophosphorus compounds, triazines, phenoxycarbon acids, organometals, carbamates, pH and chlorides are common subjects for monitoring.

6.2.4. Irrigation return flow

Long-term irrigation as a source of non-point pollution frequently causes water salinization, above all in arid or semi arid areas. The chemical composition of return flow depends mainly on the irrigation procedure, especially when liquid fertilizers or soil additives are added to the irrigation water or when waste water is used for irrigating. It also depends on the evapotranspiration rate and groundwater level. The following components are usually monitored: pH (soil and groundwater), conductivity, hardness, sodium, potassium, calcium, magnesium, chlorides, boron, sulphates, nitrogen compounds and selected groups of pesticides.

6.3. MONITORING SYSTEM

Different methods for the design, operation, data acquisition, transmission, processing and analysis, and implementation of groundwater quality monitoring systems are used depending on the purposes and objectives of monitoring. A simplified monitoring system is shown in figure 6.1.

Some of the above components of a monitoring system are described in more detail below.

6.3.1. Delimitation of the monitored area and design of the monitoring system

The nature of agricultural pollution sources and the degree of aquifer system vulnerability are the decisive factors for delimiting the areas to be monitored, and for establishing the density of the monitored network, the number of monitored parameters and the period of monitoring.

Local pollution sources such as silage effluents and liquors, stock-piles of manure and soil additives, deposits of solid and liquid inorganic fertilizers and pesticides are easily identifiable and assessable. A local monitoring system, usually temporary, is sufficient. Application of fertilizers, particularly nitrogenous, and of pesticides, and irrigation of extensive farmland areas may become a source of non-point pollution of a hydrogeological system. Here the design of a regional, long-term monitoring system coordinated with a regional or national monitoring programme and integrated with hydrological and meteorological networks is desirable.

Before groundwater quality monitoring programmes are established in selected areas or regions, the following criteria must be formulated and information made available: objectives and purposes; extent of monitored area; natural conditions, above all climatic, hydrological and geological; prevailing agricultural activities (cereal cultivation, pastures, feedlots, etc.); kind and number of pollution sources originating from farming or other activities; potential pollution sources; use of groundwater for water supplies and agriculture;

amount of utilizable groundwater resources and their availability and vulnerability; financial resources and professional expertise of the staff designated and available for the monitoring activity.

Identification and evaluation of existing and potential agricultural pollution sources are of special importance. Records of the quantity and type of applied fertilizers and pesticides, the time and method of their application, and the crop rotation system should be evaluated several years previously, if possible. When an irrigated region is monitored, records should be evaluated of water volumes applied for irrigation and of the volume of return flow, calculated on the basis of the difference between recharge (precipitation, amount of applied water) and discharge (evaporation, consumptive use) of the relevant hydrogeological system. The quantity of animal wastes can be approximately assessed from the numbers and kinds of animals. Sources of pollution producing similar pollutants as agriculture (for example urban and rural waste disposal sites) must also be identified and assessed.

The geometry and hydraulic behavior of the unsaturated zone and the aquifer/aquiclude systems, piezometric head, groundwater flow characteristics and, in the case of regional pollution the initial and boundary conditions should be known well when designing a monitoring system. Additional hydrogeological investigations should be carried out when knowledge of the hydrogeological system is poor. Coefficients of hydrodynamic dispersion, sorption coefficient, reaction constants as well as recharge and discharge of contaminants should also be known. Existing wells may also be included in the monitoring network if geological, hydrogeological and constructional data (casing and screening) are available. Because there exists in the unsaturated and saturated zones of aquifers a vertical hydrochemical stratification of contaminants (for example nitrates), the screening of newly bored monitoring wells must permit separate segment testing of the vertical hydrochemical profile of the hydrogeological system. Selected springs should also be included in the monitoring network as indicators of the aquifer system's natural activity. Other components

of the hydrosphere (precipitation, surface water) and the soil system should also be monitored.

In agricultural areas, the monitoring of the soil's chemical characteristics should not be separated from that of the groundwater quality. pH (in distilled water and in KCl solution), soluble ions, selected exchangeable cations, tests of nitrification (actual, potential, and after a week's incubation) phosphorus and boron are recommended for regular monitoring, and also triazine, organophosphates, heavy metals and phenoxycarbon acids. Variability of the soil's physical characteristics (hydraulic conductivity, water content, porosity, etc.) should also be observed.

6.3.2. Data acquisition

An essential aspect of a groundwater quality monitoring system is the acquisition of data covering sampling point locations, sampling procedures, sampling frequencies and selection of parameters for monitoring.

Sampling point location

The location of sampling points and the density of monitoring stations in the studied area depends on many factors (see 6.2. and 6.3.1.). No generally valid standards for the number and density of monitoring points per unit area (for instance square kilometer) can be defined. The density of monitoring network points around local pollution sources is always greater than in case of non-point pollution. Monitoring boreholes are usually situated close to point pollution sources, and are often temporarily used for the abstraction of pollutants and polluted water.

Vulnerability of the hydrogeological system plays an important role in the location of sampling points. Shallow unconfined aquifers with a high groundwater table are much more likely to be contaminated than

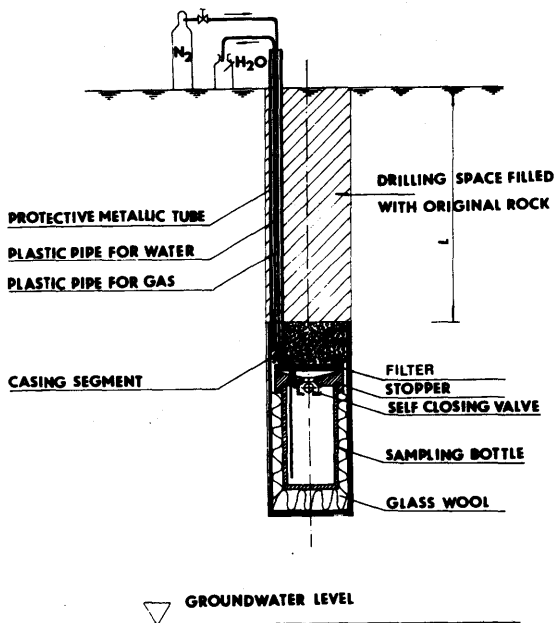
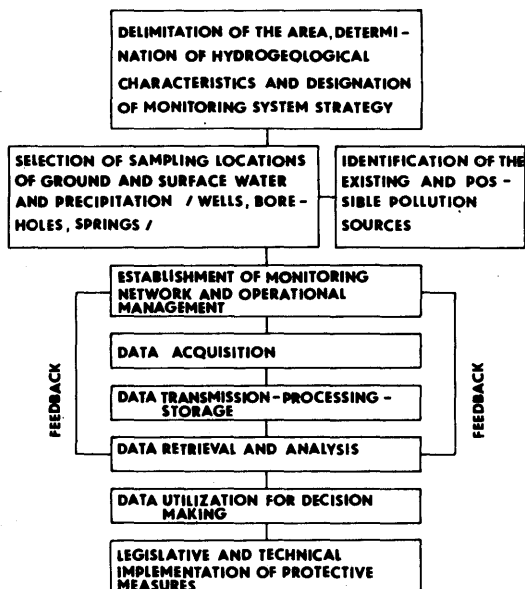


Fig. 6.1. Monitoring system.

Fig. 6.2. Sampling of water in unsaturated zone by injection of compressed gas.

confined aquifers separated from the source of pollution by an impermeable layer, or aquifers with a thick overlying unsaturated zone. In the former case the density of monitoring points is therefore substantially greater, and wells are drilled, cased and screened throughout the entire profile of the unsaturated and saturated aquifer.

In the case of confined aquifers naturally protected by an impermeable layer, monitoring wells must be very carefully drilled so as to avoid interconnection between the pollution source and aquifer via the well. It is always difficult to localize monitoring points in rocks with fissure permeability, particularly metamorphic and volcanic rocks of low permeability. When designing a monitoring network it is useful to determine the orientation, geometry and permeability of fracture systems using geophysical and geostatistical methods and assessing the vertical hydraulic conductivity.

A special approach is required when a monitoring system is being established for a contaminated aquifer in which a water supply system is located. The monitoring network must then cover recharge and vulnerable areas of the aquifer as well as existing and potential sources of agricultural or other pollution in these areas. Here it is usually necessary to identify the real source of pollution and to control and monitor farming activities.

Some monitoring points should be located in areas unaffected by human activity for control purposes. This is especially important when the regional protection of the groundwater system is studied. Movement of the contaminated zone and its front must be observed by the monitoring system. Non-point pollution sources in particular (application of nitrogenous fertilizers on a regional scale) require operational management of an extensive monitoring network. In these cases remote sensing monitoring methods may be useful. For instance, using aerial multispectral photography and geobotany, locations with overfertilized vegetation are well identifiable and measures for the protection of groundwater quality can be immediately adopted. Fast and inexpensive remote sensing methods provide more accurate data on the

pollution of the hydrogeological system, and, as part of the monitoring activity, help to make the localization of the monitoring network points more precise.

Sampling procedures and techniques

The selection of sampling procedures and techniques depends on the properties of the hydrogeological system (lithological structure and thickness of the unsaturated zone, aquifer confined or unconfined, etc.) and on the type of contaminant. The average or mixed sample from the aquifer is not considered to be valid (suitable and representative) for the study of contaminant hydrogeology problems. An average sample is only suitable to obtain general information on the areal distribution of contaminant (for example nitrogen compounds) and helpful in the initial stage of the monitoring activity when the project for establishing a groundwater quality monitoring system is being prepared.

Separate samples from different depths of the unsaturated and saturated zones are required for monitoring a hydrogeological system. Special well construction and sampling techniques are therefore employed in the study of the vertical hydrochemical profile.

Sampling methods depend on well construction, i.e. whether a monitoring well is specially drilled for sampling or for some other purposes (usually for water supply). Domestic wells are included in a monitoring system only exceptionally. Pipes and screens made of PVC are not suitable for monitoring organic contaminants, such as pesticides. Water from non-flowing wells is sampled by means of pumping, gas injection or suction. The two last techniques call for special well construction. When non-flowing boreholes are sampled, the short-term pumping for one to three hours of a small quantity of water prior to sampling itself is recommended.

Sampling techniques in the unsaturated zone

Monitoring the vertical movement of water and contaminant in the unsaturated zone is an important part of a monitoring programme. The transport of nitrates should always be monitored in regions of intensively - managed arable land. There are different methods of sampling in the unsaturated zone, some of which are listed below:

- a) Lysimeters are most convenient for monitoring in the top part of the unsaturated zone.
- b) Centrifugal extraction of interstitial water from core samples obtained from different depths during the drilling of the monitoring well. These are transported in sealed polyethylene bags (to prevent evaporation) to the laboratory. When this method is employed a new monitoring well must be drilled in each sampling period.
- c) Water is sampled from different depths of the unsaturated zone by means of compressed gas injection.

This sampling technique (see fig. 6.2.) requires the drilling of a separate borehole to a particular depth of the unsaturated zone for each sampling device. At the final depth of a borehole a casing segment is placed, with a length of 1 to 1.5 m and a diameter of 200 to 250 mm, with a sealed bottom. In the lower part of the casing segment a permanently fastened sampling bottle is placed, protected from damage, for example by glass wool.

To the casing segment a small-diameter metal tube is fastened, through which two plastic pipes are passed from the bottom and top of the sampling bottle (sampler) to the surface into a larger-diameter protective metallic tube anchored in a concrete packing ring. The space above the screen segment is again filled with the rock material which has been dug out during drilling. In the top part of the sampler is an aperture with a self-closing valve through which water flows into the sampler. A funnel-shaped stopper is fastened between

the top edges of the sampler and the screen.

Water which moves vertically through the unsaturated zone is intercepted by the stopper and accumulates in the sampler from which it is evacuated by injecting a compressed inert gas led through a plastic pipe from the surface to the top part of the bottle. By using several wells of different depths in a single locality, the movement of contaminant and water through the vertical profile of the unsaturated zone can be monitored.

Sampling techniques in the saturated zone

Methods used for sampling the saturated zone depend on the complexity of the aquifer system (single or multi aquifer system), heterogeneity of the aquifer and its type (confined, unconfined). The principal monitored factors are horizontal and vertical distribution of contaminant and the direction and velocity of contaminated groundwater flow. With agricultural pollutants the degree of contamination usually reduces with the depth of the aquifer. Monitoring is particularly focused on shallow, easily vulnerable aquifers. A monitoring system helps to determine a contaminant's transport parameters, particularly dispersion and diffusion, and the transformation processes affecting concentration and mobility of contaminants in the aquifer system.

Listed below are sampling techniques most frequently used for monitoring the hydrochemical profile of aquifers:

a) Sampling by means of packer techniques. Water is sampled by pumping separately from each of the well's screened segments closed by a packer for the period of sampling. When sampling is completed the packer moves against the next screened segment. On the outside wall of the well the screened intervals are separated by a natural or artificially emplaced impermeable material. This sampling technique is employed for anisotropic aquifers with separate groundwater subflows or wells, which at different depths of crystalline rock, intercept fractured zones.

b) Sampling from multi level screened segments. Inside the well's casing and screens are two or more small-diameter tubes reaching to different depths. Each of the tubes ends against one of the screen segments of the pilot well. Inside the well the tubes are permanently insulated by a concrete or clay impermeable material. Their bottom parts are screened, which permits separate sampling from different depths of the aquifer. Water is evacuated from individual screened intervals by means of pumping, compressed gas injection (in this case, in each screened interval a sampler with two plastic pipes leading to the surface must be available), or suction. For the suction method a special well construction is useful (Pickens et al., 1978). Small screened boxes protrude from the casing tube at different depths outside the monitoring well. In case of vertical flow in the aquifer this way of sampling may not yield representative samples. Multi level screened wells meet the needs of temporary monitoring systems. After a certain period of time the impermeable insulation separating the screened segments may be damaged.

c) Sampling from a well fully screened throughout the entire thickness of aquifer. With the use of two pumps small amounts of water are pumped from the bottom and top parts of the aquifer. This sampling technique is suitable for anisotropic aquifers with horizontal groundwater flow.

d) A costlier but technically less demanding method is to sample from several wells of different depths located in one place. The screen segments are always in the bottom part of each well. Sampling is simultaneous when all of the monitoring wells are pumped at the same time, or separate when they are pumped one after another.

e) Sampling from different depths of the aquifer using a special sampler which opens at a predetermined depth. This method can only be recommended for anisotropic aquifers with a high transmissivity and horizontal groundwater flow.

f) Various types of multistage water samplers preventing air contact with the water samples have been developed, some of them based on an original design, and are being successfully employed for monitoring in contaminant hydrogeology (Andersen, 1983; Říha, 1981, figure 6.3.).

The monitoring of changes in the vertical profile of an aquifer is apparent from figure 6.4. The construction of monitoring wells allows sampling in four separate segments of the aquifer profile. In the first well (fig. 6.4.a) the nitrate content decreases rapidly towards the level to which anthropogenic influence has not yet reached.

Contamination of an earlier date exists exceptionally at greater depths of the aquifer due to lithological conditions (fig. 6.4.b). The slow vertical flow in the aquifer was monitored using tritium analysis; values obtained are denoted as T.U. - Tritium Units.

Sampling frequency

Sampling frequency is yet another aspect of a data acquisition system. There are many reasons for the fact that the sampling frequency cannot be unified: cyclic natural processes (long-term climatic changes, the annual cycle, diurnal cycles); random processes (natural catastrophes or those caused by man such as accidental spills of hazardous contaminants); systematic processes (long-term impact of the increasing quantity of fertilizers on groundwater quality); natural conditions, above all climatic, hydrological and geological kinds of contaminants and their properties; objectives of the monitoring system; and financial resources - all these must be taken into account when the sampling frequency is being defined. The period of hydrochemical processes and variation cycles may be frequently so long that during short-term monitoring certain changes may appear to as to be random. However, they are actually part of a long period cyclic process. Thus data representativity grows with duration and frequency of monitoring.

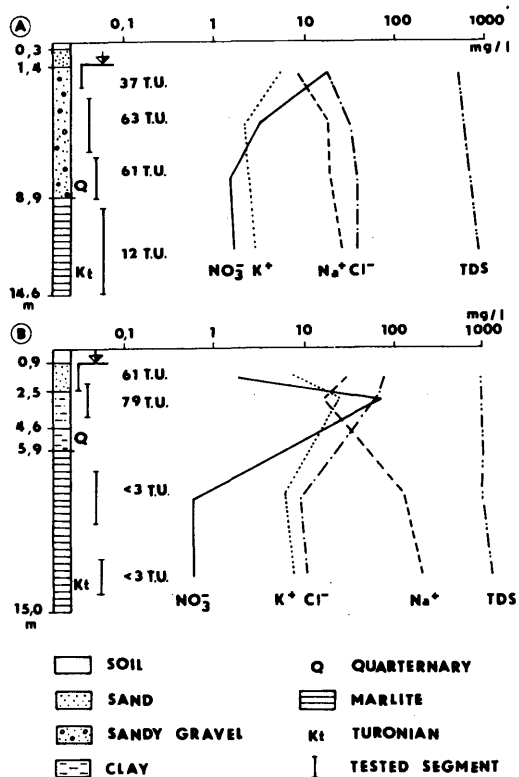
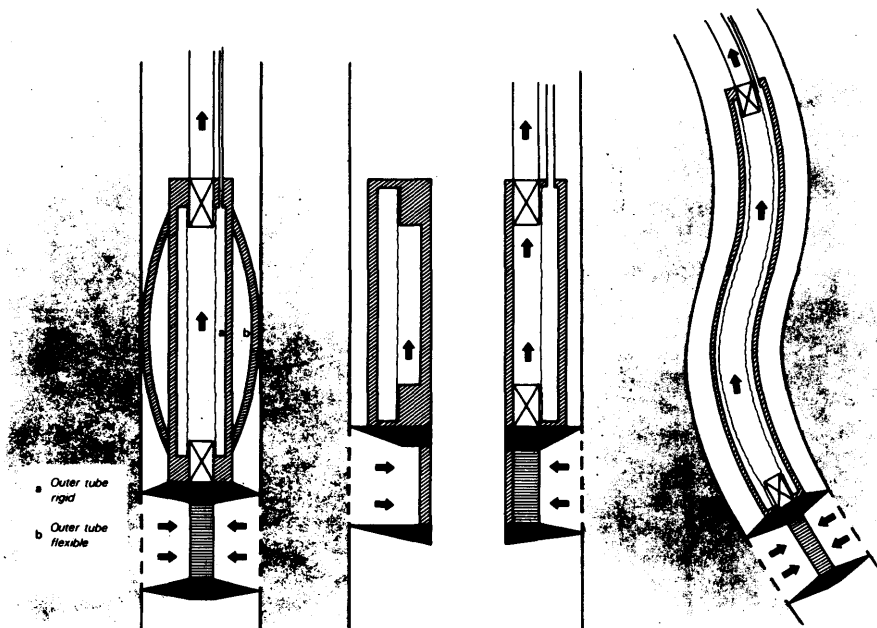


Fig. 6.3. Multistage water sampler liquid pumping device (from Ríha, 1981).

Fig. 6.4. Vertical profile of selected chemical components in shallow aquifer (from Skořepa, 1985).

In the initial stage of a monitoring programme sampling is generally more frequent, at week-, day-, or hour-long intervals; as an exception, some of the components may be monitored continuously. Later, when the contaminant movement mechanism and the variability of groundwater quality have been determined, the monitoring frequency is adapted. In national groundwater quality monitoring systems biannual sampling is usually sufficient. Sampling is commonly carried out in several vertical sections of aquifer simultaneously. In regional/local monitoring networks the sampling frequency should be higher. When determining the monitoring frequency consideration should be given to the fact that the movement of contaminant under normal hydrogeological conditions is rather slow. The frequency also depends on the type of contamination: isolated contamination (accidental spills), long-lasting uncontrollable underground leakage of liquid wastes (stock-piles of manure, septic tanks, etc.), or systematic regional contamination (incorrect use of fertilizers). Soil samples and measurements should also be taken several times a year when the agricultural impact on groundwater quality is studied, and so should geobotanic and photographic observations.

For scientific, technical and financial reasons it is customary to determine physical and biochemical parameters of water and pollutant in situ, directly at the testing locality in the field. For this purpose continuous flow quality testers or continuous sampling apparatus are the most suitable. This type of monitoring precludes or reduces the impacts of air contact, temperature changes, pH and pressure on physical and biochemical changes of the water sample which occur during its transport to the laboratory. Water quality data obtained with the help of such testers or apparatus may be simultaneously recorded and transmitted in a computer-compatible form for processing.

Automatic data acquisition field systems are recommended for pilot monitoring stations.

Various field devices and methods have been developed for identification and analysis of selected contaminants and certain hydrochemical

components in situ; however, many contaminants, such as heavy metals, toxic elements, pesticides etc., must be analyzed with the use of special precision devices in laboratories.

The transport of samples in specially designed boxes to the laboratory should be quick, with unstable components fixed. Use of standardized laboratory analysis procedures and recording forms for laboratory and field analyses and measurements is recommended for the subsequent computer evaluation.

6.3.3. Data transmission, storage and processing

Three different techniques of data transmission are recognized. When less sophisticated monitoring instruments have been installed and either a manually operated or computerized system introduced, a so called off-line system is used. Collected data have to be transferred to punch cards, paper/magnetic tapes or magnetic discs. Since rewriting and punching of data from graphical or digitized records are required, substantial errors can be expected and a thorough checking of data is needed before they are utilized for further analysis.

More advanced systems monitor data on-line, with the storage medium usually being a magnetic tape which is periodically processed together with other tapes on computer. Here errors are normally limited to failures of monitoring sensors, flat batteries powering the movement of tapes, and the like.

Up-to-date on-line systems are hooked to the computer via telephone lines or radio transmission. There is a future for on-line systems utilizing satellite transmission. Gaps in transmitted data can always be expected caused by a temporary failure of transmission. It is therefore strongly advisable to preserve some of the less sophisticated forms of duplicate recording at each monitoring point.

In every case, some form of regional data base for all components monitored within the region ought to be organized from the initial stage. Before being entered into the base, all data should be verified as soon as possible after they have been transmitted, and all gaps filled in cooperation with the personnel responsible for local

monitoring. A similar procedure is recommended when a national monitoring system is the subject of evaluation. Here cooperation with persons in charge of regional monitoring is desirable.

Automated data transmission is not available in most local, and sometimes regional monitoring systems. With regard to the subsequent conversion of data for storing in a regional data bank it is emphasized that the reporting monitoring forms be standardized and unified.

Data from an established regional monitoring system also include data from national or local monitoring systems, data from water users, etc. Data collected at different times using different methods of measuring, sampling and analysis need not be always comparable. Therefore one of the designers' very important tasks is to process those data and to balance data coming from different sources. When processed, these data are also stored in the given monitoring system's regional data bank.

When monitoring agricultural impact on the water quality, account should be taken of the considerable variability of processes going on in time and space within the agro-eco-hydro system between vegetation-soil-rock and groundwater. This calls for a frequent updating of the monitoring system, an easy access to the data bank, and a fast procedure for record and data retrieval. Data files are not usually large because most agro-monitoring systems operate for a limited period of time on a local or regional scale. Allowing for the above requirements, the random and inverted list organizational concepts of data files are considered to be technically and financially the most advantageous (Everett, 1983).

6.3.4. Data retrieval and analysis

Data retrieval and analysis are very important steps in the process of monitoring. At this point the decision must be made in which numerical and graphic outputs and information on time and space changes occurring within the monitoring area will be submitted to the users.

Data retrieval is closely related to the objectives of the monitoring programme, in our case the impact of agricultural activity on the hydrogeological system. Information output differs depending on the users of the data. Retrieval procedures should differ for the agricultural sector, water sector and the sphere of ecology. Integrated and interdisciplinary information processing calls for decisionmakers and planners handling wide-range analysis of the agro-eco-hydro system, including economic, social, ecological, legislative and, last but not least, political aspects.

Data retrieval for individual users (for example farmers or water users) is generally in the form of simple, easy to understand, practical and inexpensive information. Assessment of the impact of agricultural activities on one water supply system and on the water resources in the monitored area within an integrated system controlled by natural processes and anthropogenic activities, requires the employment of complex statistical analysis. The quality of statistical operations depends above all on the representativity of the set of data under study, which grows with duration of monitoring and the amount of data available. From the selected data files systematic errors must be eliminated, while they may contain random errors which do not affect the results in any significant way. Common statistical calculations include those of the mean values, standard deviation and reliability interval, the latter being of a special significance in contaminant hydrogeology.

Extreme values of results are excluded from the mathematical expression of relationships between variables - for instance results subject to gross errors, incorrect sampling etc. Relationships between variables are categorized as functional, regressive or correlational. Functional relationships can be used to describe natural processes, and thus also the hydrogeological system, only exceptionally, as the monitored quantities are variable and random. Correlation and regression are stochastic relations, both of them commonly used for analyzing the qualitative relations within the agro-eco-hydro system. In view of the close interdependence among variables, correlation is of

a special importance for dealing with anthropogenic impacts on the hydrogeological system.

Statistical operations based on data obtained from groundwater quality monitoring generally include:

statistical distribution of monitored values; calculation of position parameters - arithmetic, geometric and weighted mean and median; calculation of scatter parameters - standard deviation, coefficient of variation; correlation and regression calculations for selected physico-chemical components of water and contaminant - regression curves, regression and correlation coefficients, factor analysis - calculation of statistically selected relations between hydrochemical and hydraulic parameters of the hydrogeological system and within the vegetation-soil-water system; trend analysis - calculation and graphic interpretation of the trends of changes in physico-chemical components of water and contaminant in space (distance and depth); harmonic analysis - expression of periodic changes in time of the physico-chemical composition of water and contaminant.

Feedback is a common feature of the monitoring process during data analysis. In this stage modifications and changes are introduced, for instance in the design of monitoring, sampling frequency, etc.

Evaluation of the monitoring process, conclusions and recommendations for future operation of monitoring systems are described in the final monitoring report.

6.3.5. Data utilization for decision making

Financial expenditure on the design and operational management of monitoring systems is not always used to best effect. The result of monitoring are usually published or are accessible in data banks, but not always used for practical purposes. The reasons for this may consist in an underdeveloped governmental or regional organizational structure, poor information or communication systems or, in less developed countries, a shortage of specialists able to apply the

results provided by the monitoring system; etc. It is therefore a generally accepted concept that a monitoring system is beneficial only when the results it yields are applied.

It is most important to transfer knowledge gathered from monitoring activities in a form that can be used by decision makers. In other words, the analysis of monitoring data should be interpreted in a form intelligible to specialists responsible for solving problems of society.

Taking into account the results of monitoring data analysis as well as the economic and social implications, the task of decision and policy-makers is to choose a suitable strategy, to define priorities, preferences, conflicts, interests and risks involved in the exploitation of natural resources in a given region, to find a way of incorporating regional monitoring data into a long-term national water policy, to adopt charging principles and measures for the protection and control of groundwater quality, and to establish a management methodology for the agro-groundwater system.

6.3.6. Legislative, administrative and technical implementation of protective measures

The legislative, administrative and technical implementation of protective measures is based on the results obtained from groundwater quality monitoring systems and it is, in a certain sense, the concluding stage. Functional, organizational and governmental structures, above all institutional, as well as technical and control instruments and legislative measures based on Water and Environment Acts are essential for implementing results obtained by monitoring qualitative changes and variability of the hydrogeological system as related to agricultural activities. Governmental and control authorities set up strategies and are responsible for groundwater protection as an integral part of national and regional water management policies and water management plants.

The last two stages in a monitoring system programme briefly described in chapters 6.3.5. Data utilization for decision making and 6.3.6. Legislative and technical implementation of protective measures are already closely related to the question of agro-groundwater system policies, strategies and management.

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7. CONTROL AND MANAGEMENT OF AGRICULTURAL IMPACT ON GROUNDWATER

V. KOLAJA, J. VRBA, K.H. ZWIRNMANN

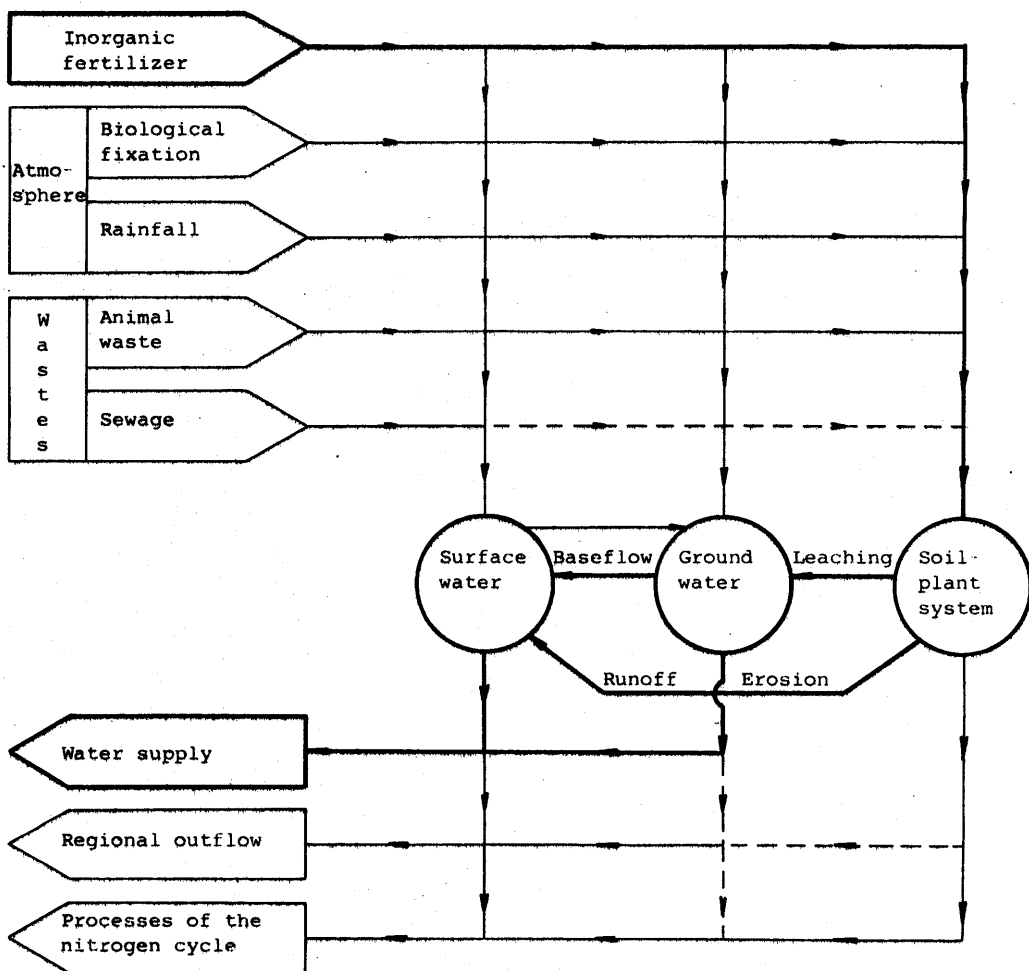
7.1. INTRODUCTION

Control and management of the agro-hydrological system is a complex task of general interest and great practical importance. It requires comprehensive analysis of the physical and socio-economic aspects of all agricultural impacts affecting the groundwater resources, adoption of a system approach, and a methodological framework for analysis (especially monitoring and modelling) and control.

Soil and water are renewable and, for the most part, vulnerable natural resources. They are distributed irregularly over the Earth, like the human population. The soil environment is the chief source for food production, and water resources yield drinking water. Food and water are of top priority for mankind, and the need for them steadily increases. On the national, regional or local scale soil and water may bear different values for society (e.g. regions with abundant farm land and shortage of water, or vice versa), which may lead to conflicts between the agricultural and water sectors. In such a case the main objective is to develop an approach to the analysis and evaluation of management alternatives to control pollution originating from agricultural impacts on groundwater resources, and to define optimization multicriteria for the given regional agro-hydrological system. Nitrate and pesticide pollution control systems for groundwater resources are outlined.

7.2. NITROGEN AND WATER RESOURCES - OUTLINE OF A MANAGEMENT AND CONTROL SYSTEM

The schematic representation of the inputs and outputs of nitrogen to and from a regional water resource system (Fig. 7.1.) conceptualizes,



- Major paths of nitrogen in the system
- Less significant paths of nitrogen in the system
- System parts of particular relevance to chapter 7

Fig. 7.1. Schematic representation of the inputs and outputs of nitrogen to and from a regional water resources system.
(Source: adapted from Reeves, 1977)

in a highly simplified manner, the physical system requiring control.

The amount of nitrate present in water abstracted for supply is determined by the amount of nitrogen lost from the system as regional outflow. However, it is basically controlled by the various processes taking place in the nitrogen cycle, particularly by the interaction of water with the soil-plant system. Consequently, the system to be controlled has been divided into three generalized parts; surface water, groundwater, and the soil-plant system.

The major inputs of nitrogen to this system are:

1. waste sources such as domestic and industrial effluent, and animal wastes;
2. atmospheric sources, such as nitrogen in rainfall, and biological fixation;
3. inorganic fertilizers.

In addition to these sources, the indigenous nitrogen potential of the water resource and soil-plant systems must be taken into account. Of prime concern is the control of non-point pollution sources in agriculture, such as organic and, especially, inorganic fertilizer. Hence the system must provide a framework for analysis of the various factors affecting regional water resources management. In order to understand how water supply and its management is influenced by increasing nitrate concentrations in water resources and how to ensure a safe drinking water supply, planners must link land use with water supply development. The framework for analysis follows the concept of a decision-making process based on the control system shown in figure 7.2. The major components considered are:

- a) The system to be controlled, encompassing
 1. regional authorities, representatives of the general public which are supplied with water and agricultural commodities and govern the overall control system by setting the management objectives; they also contribute to nitrate pollution of regional water supply sources through the disposal of human and industrial wastes,

2. the environment, especially the atmosphere, which provides the background load of nitrogen to the two environmental systems of interest, the soil-plant system and the water supply sources,
 3. the water supply and management agencies managing the water supply sources and responsible for ensuring a safe drinking water supply,
 4. the agricultural sector which strives to maximize production, causing nitrate pollution of water supply sources as a side effect of technological activities of crop production and waste disposal to the soil-plant system.
- b) The management objectives of the overall control system which should be accomplished through management measures appropriate for the specific system.
- c) The management subsystem, where management objectives are achieved through planning and implementation of management measures not only in the field of water supply and management, but also in the agricultural sector.

The components of the system to be controlled (the regional authorities and the environment, with its subcomponents of the water resource system and the soil-plant system) are physically connected by mass flows (nitrate polluted water, drinking water, agricultural commodities) and constitute the basis and target for decision making. In contrast, components of the management subsystem are linked by the flow of information. The link between these two main parts of the overall control system is provided through the implementation of management measures.

A water management agency needs at least three types of information before strategic planning decisions for pollution control can be taken:

1. identification of the relative importance of nitrogen sources and those supply sources most at risk from nitrate pollution,
2. predictions of likely future levels of nitrate concentration in supply sources,
3. identification of implications to water supply development plans by assessing the effects of management alternatives to be taken.

Social benefits can be gained if the benefits from intensified agricultural production outweigh the additional costs of regional water supply. This statement suggests the need for identifying the interdependence between the economic and physical systems so that the effect of public policy decisions on natural resource use and environmental quality can be determined. From the viewpoint of resource economy and planning, it can be said that water pollution control must be coordinated with water resource development and land use planning to achieve a better allocation of natural resources.

Economic effects may be direct or indirect. Direct benefits from improved water quality can be obtained through reduced or avoided water treatment costs, reduced medical costs, etc. Direct costs, which can even include reduced agricultural production, are incurred by farmers as a result of pollution control. Other direct costs include the cost to regional water supply agencies of providing water treatment facilities. It should, however, be noted that indirect effects, resulting from the sensitivity of the highly interdependent national economy to production changes, can exceed direct costs and benefits to a single producer. Generally, the distribution of benefits and costs is accepted as the most important effect of pollution control.

Other important effects relating to the institutional aspects of implementing control strategies usually require additional accounting, monitoring, reporting, supervision, enforcement and management.

Moreover, to be effective, a control strategy must be flexible enough to adjust to changing economic and physical conditions.

7.3. CONTROL OF GROUNDWATER POLLUTION

The control of groundwater pollution resulting from agricultural activity is a task requiring the integration of many aspects of both the agricultural production system and groundwater resources development. Any comprehensive agricultural pollution control programme must therefore link investigations of the agrobiological and hydrogeological system. Because of differences in the climate, soil, rock composition, geological structures and their hydrogeological properties, and farming practices on a regional scale, no standard control measures can be applied. Nevertheless, some general principles in the approach to solve the problem can be recommended.

When considering the methodology of investigating the hydrogeological system and agricultural activity, four main criteria must be considered:

1. the areal extent of the contamination process (point vs. non-point pollution),
2. the capacity of contamination (potential vs. real contamination),
3. duration of contamination (temporary, long-term, old or recent) and
4. aquifer vulnerability (shallow, deep, insulated by impermeable layer).

Since many agricultural activities produce irreversible pollution of groundwater, and water quality rehabilitation techniques are ineffective in many cases, the stress in agricultural groundwater pollution is placed on prophylactic protection.

7.3.1. Preventive groundwater system protection

The initial step in the preventive phase of pollution control is assessment of the groundwater system vulnerability to contamination caused by farming activities. Since the contamination process is strongly influenced by hydrogeological characteristics of the soils and rocks in the recharge (and most vulnerable) area of the groundwater system, investigation begins by identifying these areas. Conventional hydrogeological methods, like hydrogeological mapping, measuring of soil and water characteristics, remote sensing, etc. are employed to carry out this task.

The role of the agro-biological part of investigation is to identify:

1. potential sources of agricultural pollutants,
2. physical, chemical and biological characteristics of potential pollutants,
3. potential zones of contact between the agricultural and the groundwater system,
4. the probable mechanism of the potential pollutants' release from the agricultural into the groundwater system, or
5. feasible methods to reduce adverse effects of pollutants on human health.

The objectives of the hydrogeological part of investigation are:

1. to find the present level of quality of the groundwater system and to separate natural and anthropomorphic processes affecting this system,
2. to identify non-farming sources of pollutants identical with potential agricultural pollutants,
3. to assess climatic and hydrophysical parameters of soils and rocks in the recharge area,
4. to determine and characterize zones of contamination risk and vulnerability of the aquifer.

In principle, methods of agro-hydrological system investigation are based on monitoring programmes (see Chapter 6). The results of investigations are best presented by groundwater protection or other spe-

cialized hydrogeological maps (Landreau, 1982). A preventive control system is thus a synthesis of agro-biological and hydrogeological investigations and the optimum integration of the competing water and soil users' interests, i.e. those of the water supply and agricultural sectors. Preventive control systems comprise above all:

1. delimitation of groundwater resources protection zones,
2. specification of protective measures,
3. water quality monitoring under different agricultural conditions.

Protection zones are usually identical with an aquifers' high contamination risk zones, but they should also reflect agricultural administrative boundaries to allow application of the prescribed preventive measures.

The best way to prevent groundwater pollution is to identify and isolate pollutant sources from the geo-environment. Such measures are effective only with point pollution sources (concentrated livestock, fertilizer and pesticide deposits, etc); they are unrealistic in the case of non-point sources of agricultural pollution (free-ranging livestock, spreading of fertilizers and pesticides over farmland on a regional scale, etc.). The objectives of control, i.e. to prevent widespread agricultural pollution, are attained through restrictions and, in certain cases, the complete prohibition of some agricultural activities, such as the limitation of the amount and kind of applied (above all inorganic) fertilizers together with strong pest management and policies (use of degradable and environmentally inactive pesticides).

An integral part of a preventive control system is the establishment of a groundwater quality monitoring network and regular observation of selected data on water quality. The design of a water quality monitoring scheme is based on the conclusions drawn from interpreting agro-biological and hydrogeological investigation results.

Preventive water quality monitoring must provide timely information especially about:

1. potential emergence of pollutant in the groundwater resources system,
2. the approximate location of the emerged pollutants source,
3. the rate of accumulation of persistent pollutants,
4. input of identical pollutants from non-agricultural sources into the groundwater resources system,
5. changes in farming practices on the recharge or vulnerable areas of the groundwater resources system.

Several aspects of the process of contamination by agricultural pollutants are still not understood well in theory, and some phenomena (for instance biodegradation of pollutants) are too complex for regional generalization. In order to prepare a scientifically-based groundwater protection control scheme, it is therefore necessary to integrate a specialized scientific research programme into the procedure for the solution of the problem.

This programme should determine the potential contamination characteristics and parameters at research sites representative of the particular region. A research programme should include measurements of:

1. dispersion coefficient for each important potential pollutant,
2. potential pollutant propagation speed in the unsaturated zone,
3. potential pollutant dilution rate in the saturated zone,
4. local biodegradation effect on each potential pollutant,
5. chemical degradation of potential pollutants in the saturated and unsaturated soil and rock environments (figure 7.3, 7.4, 7.5).

Research results are reflected in correction of the groundwater system protection zone parameters, i.e. the prescribed type of protection measures and the characteristics of the monitoring scheme.

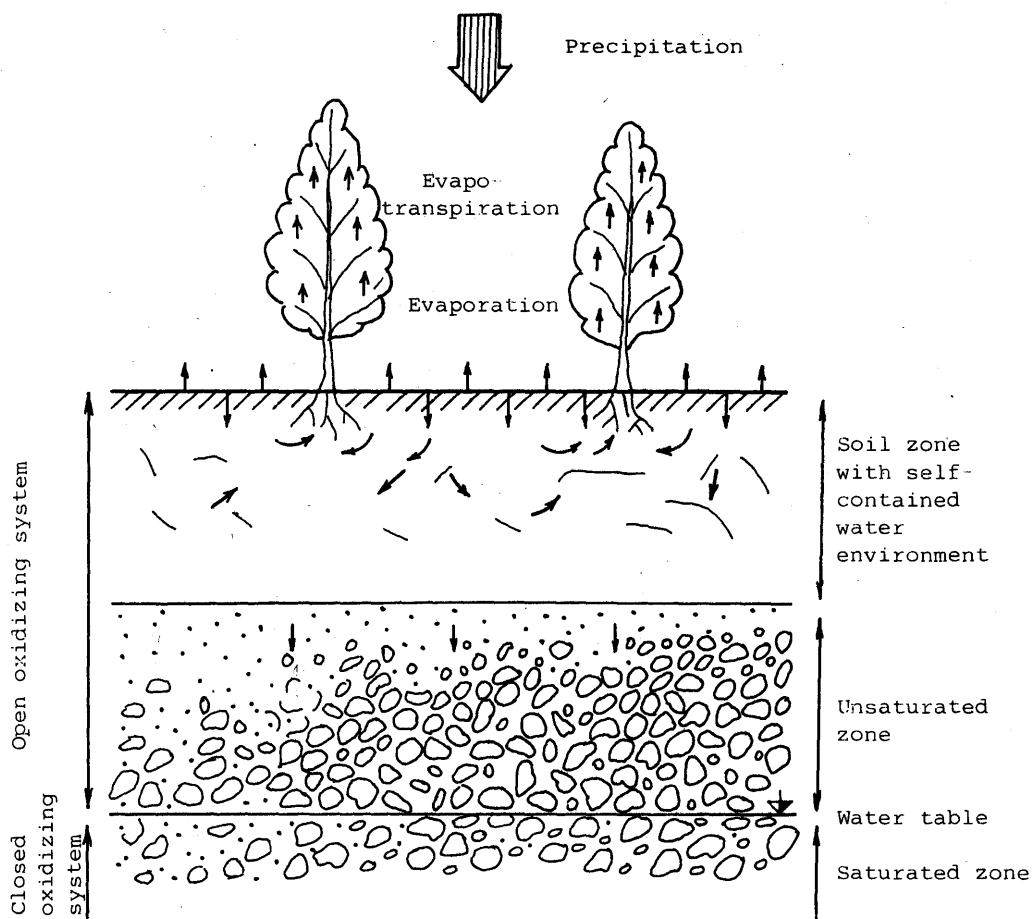


Fig. 7.3. Soils with self-contained water environment
(Alföldi, L. 1981)

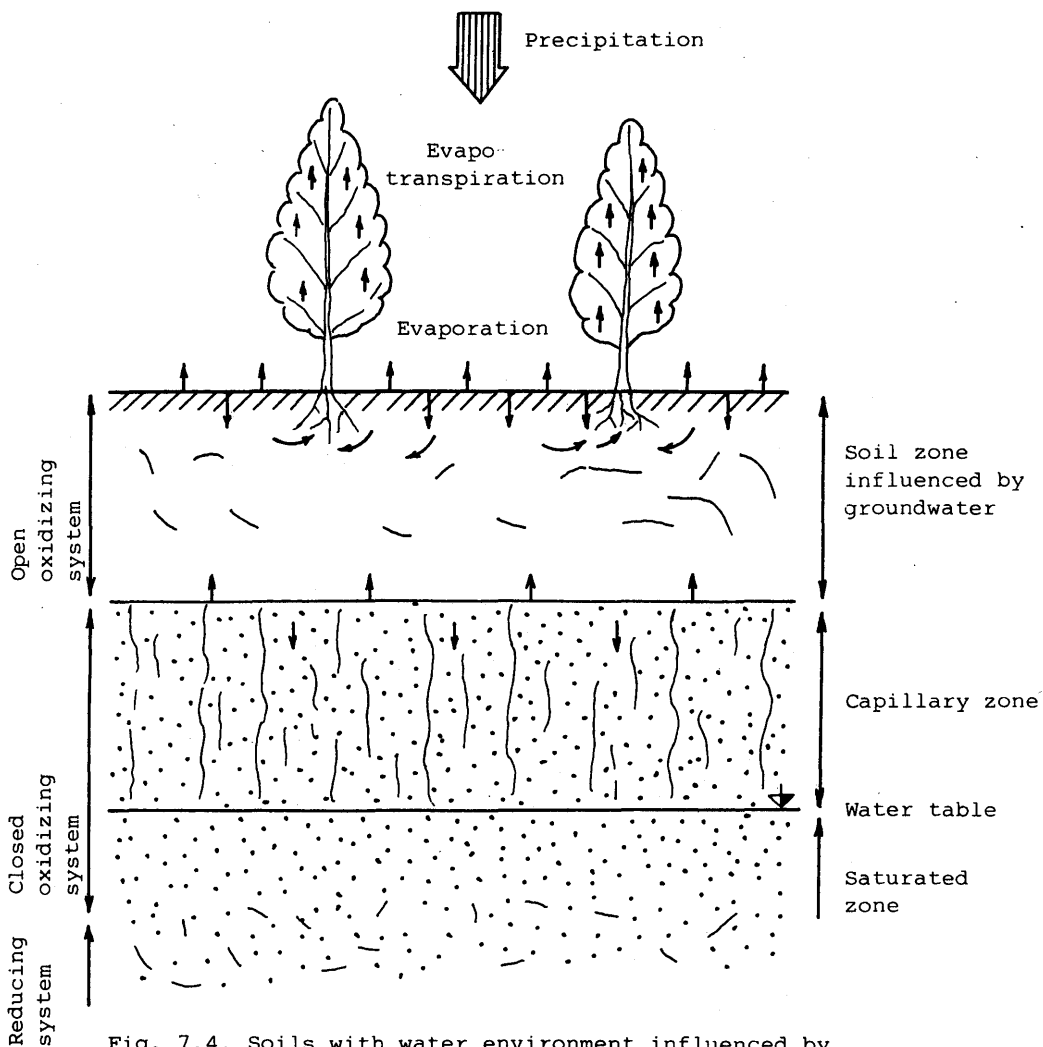


Fig. 7.4. Soils with water environment influenced by groundwater (Alföldi, L. 1981).

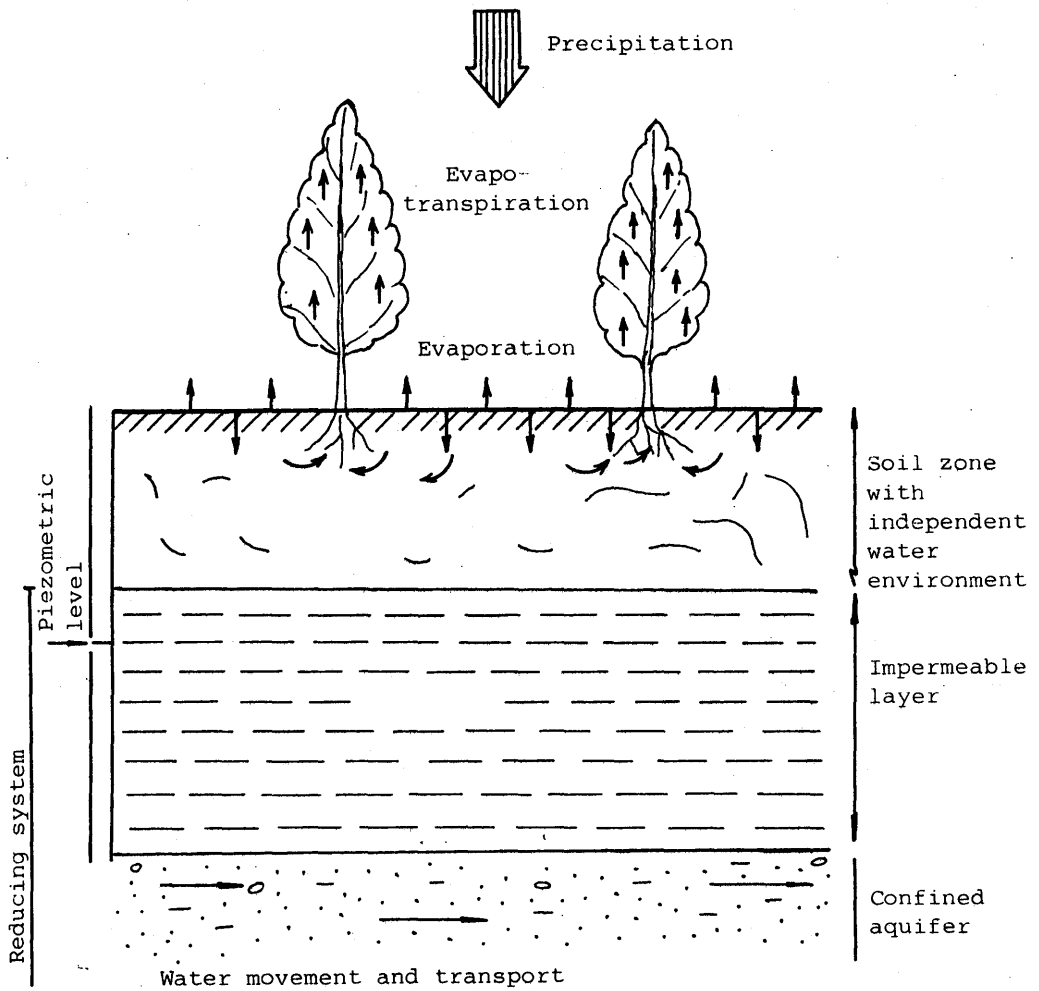


Fig. 7.5. Soils with independent water environment (Alföldi, L. 1981).

Scientific research as part of a preventive control system should further include studies aimed at optimization of agricultural production practices in respect to groundwater pollution, taking account of the climatic, pedological, geological, economic and social conditions of the region. Proper land use management, use of environmentally inactive fertilizers and pesticides, application of inhibitors controlling fertilizer and pesticide release, etc., are indirect preventive measures, highly effective mainly in controlling non-point agricultural pollution.

7.3.2. Control of pollution sources

While some parallels can be found between point, and non-point pollution control in the preventive stage of hydrogeological system protection, there is a fundamental difference between the control of point pollution and the control measures applied to recurrent widespread agricultural pollution. The pollutants encountered in point source agricultural groundwater contamination range from nitrates and phosphates derived from fertilizers, to organic substances like silage liquors or animal waste, to a large variety of pesticides. The only generally recognized non-point sources of groundwater pollution are nitrates. At this point mention should be made of the use of slurry, above all pigs slurry, as a fertilizer. Slurry is considered to be one of the most important organic pollutants produced by farming, endangering the quality of (especially) shallow aquifers. Direct application of slurry in groundwater sources protection zones is usually not permitted.

Slurry processing methods play an important role in agro-hydrological system management. For economic reasons, the prevention of deleterious effects on human health and environmental protection (including groundwater), the following slurry processing methods are recommended (R.J. Barták, 1982): activation treatment of slurry with the help of waste water poor in biogenic elements (nitrogen, phosphorus); thermophilic aerobic stabilization; composting; utilization as animal feed,

for instance the CERECO (USA) and AGROEQUIPMENT (France) methods which separate the material into a coarse, polysacharidic component (ensilaging, fertilizing, granulation), a fine protein (drying and granulation), and a mineral component (fertilizer); ensilaging; protein fortification; enzyme hydrolysis; chemical hydrolysis (at 140 to 170°C) with additives, so that sterilization and degradation of toxins and intermediate products are ensured (material thus prepared is turned into an easily separable suspension, and consumed after some treatment; this is a waste-free technology well applicable in groundwater source protection zones); anaerobic digestion, with usable biogas as a by-product; extraction of nutrients through reverse osmosis; pyrolysis (thermal decomposition of the slurry's solid component).

Non-point, and usually long-term, agricultural contamination is a source of conflict between farming interests and water supply needs. Control and management of non-point source contamination necessitates an integrated approach. The need to deal with frequent recurrence of pollutants released from the agricultural into the groundwater system over large areas obliterates the distinction between prevention and rehabilitation, because preventive measures (especially in agricultural systems) are the only practical means of ameliorating a deterioration of groundwater quality.

Point agricultural contamination is usually a time-limited problem due to the feasibility of isolating and identifying the pollutant source. Once the source is isolated, contamination can be managed mainly by hydrogeologic methods, arranged in a basic three-stage scheme: investigation-monitoring-rehabilitation. Although contamination hydrogeology involves application of an integrated set of multidisciplinary techniques (Goldberg, 1981), the management remains within the remit of water supply engineers and hydrogeologists.

Point pollution control

Comprehensive control of actual point agricultural contamination of groundwater should involve the following steps:

1. detection of the contamination source, identification of the focus of contamination and study of the mechanism of pollutant entry into the groundwater resource system,
2. isolation of the contamination source from the environment,
3. physical, chemical and biological identification of the pollutant(s) and evaluation of the quantity released to the environment,
4. analysis of hydrogeological conditions of the region and definition of the groundwater contamination risk areas,
5. design and establishment of a groundwater monitoring network to evaluate the present level of groundwater pollution and to forecast its development,
6. preparation and testing of groundwater quality rehabilitation technology.

The sequence of the above steps will depend on the contamination case in question. Control activities initiated by the emergence of a pollutant in groundwater supply will start with steps (4) and (1) in a search for the source of contamination. If the pollution begins with a reported accidental spill, the control activity will start with step (2) followed by step (4) to evaluate the groundwater contamination risk.

Methods used in completing step (1) of the contamination control scheme include hydrogeological mapping at a scale relevant to the contamination case and extent of the groundwater resource system's recharge area, collection and interpretation of data on agricultural activities, remote sensing of the surface and near-surface symptoms of the contamination, drilling of test boreholes, groundwater and soil sampling, physical, chemical and biological analysis, hydrophysical measurements, infiltration tests and tracer tests in the unsaturated and saturated zones of the hydrogeological system.

To isolate the contamination source (step 2), various measures can be applied. Depending on local conditions and the way in which the pollutant is released from the source, the most suitable method is

chosen for the complete removal of the source (including the contaminated soil underneath), or the source surroundings are isolated from the groundwater flow system by mechanical barriers (cement, concrete) anchored in the impermeable bedrock (if shallow enough), or by hydraulic barriers (if the permeable bedrock is at a great depth), or the source surroundings are separated by a drainage system (trenches, wells).

Samples for physical, chemical and biological analyses of the contaminating substance (step 3) are collected from the source itself, if it still exists at the time of investigation. When investigation starts after the source has ceased to exist, for instance when a liquid pesticide spills in a road or railway accident, it is advisable to consult the manufacturer of the contaminating substance. Taking samples for pollutant analysis from the contaminated soil, rock or water should be the last resort because of the pollutants possible physical, chemical and biological changes resulting from pollutant-soil (rock, water) interaction. Analyses of pollutants must yield data which help a better understanding of their behavior in the soil, rock and water environment (mobility, persistence, degradation), and also for the evaluation of the latent risk to the groundwater consumers' health. The physical, chemical and biological parameters of pollutants to be identified are solubility in water, size of dissolved particles, chemical composition, chemical instability, toxicity, biological composition (pathogens), etc. The quantity of pollutant released into the groundwater resources system is an important factor in forecasting the progress of contamination, designing a control scheme and selecting an appropriate amelioration technique. The first evaluation of this quantity is based on the information received from those who caused the pollution. Owing to the interests of the "defendant" in a contamination case, reliability of such information is always questionable, and the data obtained must be well examined and, if possible, made more accurate by information from other sources (for example witnesses to the accident) and substantiated by secondary evidence.

The investigation of hydrogeological conditions in the area of contamination (step 4) mostly involves conventional hydrogeological methods: drilling of boreholes, pumping tests, potentiometric measurements, groundwater sampling and quality analysis. The data obtained during the hydrogeological investigation serve to determine the groundwater system's geometry, hydraulic parameters, boundary and quality conditions. Based on this knowledge, the risk area as related to the actual contamination can be defined. It encompasses that part of the recharge area (input boundary conditions) around the focus of contamination and part of the aquifer in the direction of the groundwater flow. The extent of the risk area depends on the quantity, persistence and mobility of the pollutant released, on the permeability and thickness of the unsaturated zone in the recharge area and on hydraulic parameters and the potentiometric gradient of the endangered aquifer.

The data collected during the investigation stage of the control programme (steps 1, 3 and 4) are used as the basis for the design of the monitoring network (step 5), described in detail in the preceding chapter. The objectives of monitoring an already existing point source contamination are more specific than in the prevention stage, and include: determination of the actual extent and intensity of contamination; surveillance of the progress of contamination; and proof of the effectiveness of the remedial measures.

The sampling frequency is determined by considering the pollutant's mobility and the groundwater flowrate in the particular contamination case. The density of stations and frequency of observations are regulated during the monitoring period according to the interpretation of data obtained from the first observations. It is recommended that the pilot stations of the network should be equipped for continuous measurements of important parameters especially the quantity of pollutant.

Rehabilitation of groundwater quality in a resources system affected by point contamination of agricultural origin (step 6) is always a costly and long-term problem. The efficiency of available clean-up

techniques is usually limited, and only the contamination of a limited area is amenable to clean-up measures. Among the subsurface restoration techniques used in small-scale contamination are removal of the contaminated water from the system by pumping from wells located along the contamination front and surrounding its center; scavenge pumping in the case of clearly defined horizontal zoning of the contamination; and dilution of pollutant's concentration by artificial recharge (Jackson et al., 1980). The clean-up techniques that involve introduction into the groundwater system (by surface application or well injection) of chemicals which assist natural degradation of pollutants have to be considered case by case and experimentally tested before implementation, because the presence of chemicals can cause a new constraint and side effects on the groundwater quality.

Non-point Pollution Control

The only mass-scale occurring groundwater pollutant reported in non-point agricultural contamination cases at present are nitrates originating from organic and inorganic fertilizers applied to arable land and from ploughing of leys (Mackenthun, 1974; Robertson, 1979; Young and Gray, 1978 etc.). Compounds of potassium or phosphorus derived from fertilizers and pesticides, due to their lower solubility in water, lower mobility and lower quantities applied (in relation to nitrogen compounds) accumulate in soil and in the unsaturated zone, and so far constitute a potential threat to groundwater resources or, as an exception, remain within the local (point) contamination scale.

Non-point source contamination control systems outlined, and control measures developed and applied, are concerned chiefly with the pollution of aquifers by nitrogen compounds which results in the NO_3 anion content in groundwater exceeding the drinking water standards limits (Jackson et al., 1980; Zwirnmann, 1981; Landreau, 1982; Vrba, 1985).

The fundamental principle of nitrogen pollution prevention should be that not soil but rather plants are fertilized by nitrogen, i.e. the predominant part of nitrogen fertilizers are applied during the period of intensive growth (J. Lehocky, 1986).

Due to the great areal extent of non-point agricultural nitrate contamination, application of the "isolate source policy" and subsurface clean-up techniques in the contamination control system is impracticable. The only realistic and effective control measure leading to improvement of groundwater quality affected by dispersed agricultural nitrate pollution is to reduce the nitrate content in the recharge water of the groundwater system. Uncontaminated recharge dilutes nitrate concentrations in the groundwater system and gradually replaces the contaminated water. This process, which will restore natural groundwater quality, is very slow, mainly due to the low percolation and filtration rates (decimeters to meters per year) in the unsaturated and saturated zones.

There are two ways to reduce agricultural nitrate content in recharge water: restrict or prohibit nitrate-producing agricultural activities in vulnerable recharge areas of the groundwater system, and change (optimize in view of nitrate loss) agricultural practices and activities. The decision on the choice between the two alternatives is based mainly on economic and social factors. Both ways lead to a certain reduction in agricultural production in regions within the vulnerable groundwater recharge areas. In the decision-making process, the relative importance of groundwater resources and agricultural production for a given region or country should be considered, as should the feasibility of substituting either water supply from the groundwater system or agricultural products of that area by these items from other sources. The modern trend in developed and densely populated countries, especially in those whose water supply is dominated by groundwater, is the integrated use of farmland in groundwater system recharge areas.

Management, control and optimization of the relationship between an agrosystem and a groundwater system, with the aim of minimizing the impact of agricultural activities on groundwater quality, and adaptation of proposals for rehabilitating a contaminated hydrogeological system require a specific approach and solution in each agricultural region. Evaluation of natural conditions, type of agricultural activities and intensity of water resources utilization are particularly important. The following activities are especially emphasized in the management and control of agro-groundwater systems:

1. determination of the geometry and hydraulic properties and conditions of the hydrogeological and soil system,
2. evaluation of physical and biochemical processes in the soil environment, with special regard to the stability of the soil organic matter and the carbon/nitrogen balance,
3. investigation of climatic influences, precipitation and temperature effects on the above processes,
4. selection of suitable plants and determination of the rotation system,
5. selection of suitable fertilizers (in the case of nitrogen fertilizers preference should be given to ammonium forms of nitrogen), pesticides and chemical inhibitors,
6. determination of regulation between animal production and extension of the farmland,
7. determination of doses, times and techniques of fertilizer application,
8. determination of irrigation schemes and design of drainage systems if necessary,
9. determination of the recharge (and vulnerable) areas of the hydrogeological system and evaluation of the groundwater resources potential,
10. design of soil and groundwater quality monitoring system, vertical profiling of the unsaturated zone and aquifer,
11. study of physical and biochemical processes and solute transport in the plant-soil-hydrogeological system,
12. selection of a suitable method for modelling transport and transformation processes in the hydrogeological system,

13. evaluation of field, laboratory and model studies,
14. recommendation for changes, extent and intensity of agricultural activities, with special regard to the drinking water protection areas and/or groundwater resources protection,
15. evaluation of economic and social consequences of changes recommended for the agro-eco-system,
16. institutional and legislative implementation of designed changes in the regional agro-eco-system,
17. optimal integration of the competing soil and water users interests, i.e. the water supply and agricultural sectors.

These are the most important aspects of non-point agricultural nitrate pollution control. However, other relevant aspects of direct and indirect control, for instance development of new types of inorganic nitrogen fertilizers, application of nitrate release inhibitors, developments of new types of crops etc. are not included so as to keep the control system within manageable limits. The complexity of the control system and, particularly, the need for cooperation between the two different economic sectors (water supply and agriculture), imply the system approach and the use of modern tools of system analysis and management, including suitable mathematical models (Chapter 5).

7.4. PESTICIDES - OUTLINE OF A MANAGEMENT POLICY

Pest management, control and policy are today some of the most important tasks of agriculture in the sphere of ecology. Reducing environmental side effects of pesticides requires: licensing policy for the production of new types of pesticides; pest management with special emphasis on preventive, integrated protection of crops and soil; control measures based on monitoring and information systems and warning signals; adequate laboratory instrumentation; development of rapidly degradable and environmentally inactive pesticides; development of biological and biochemical protective substances; and research into the interaction and mechanism of pesticide movement in

the soil-groundwater systems.

The effects of pesticides on the hydrogeological system are governed mainly by:

1. kind, properties and amount of pesticides and their potential to leach through soil to groundwater,
2. weather at the time of pesticide application, application techniques and/or irrigation intensity,
3. type of vegetation and its ability to take up water through the root zone,
4. soil physical and chemical properties, soil structure and texture, amounts of organic matter and clay material, soil-water potential and hydraulic conductivity,
5. vulnerability of the hydrogeological system, thickness and permeability of the unsaturated (vadose) zone and type of aquifer (phreatic, semi-confined and confined), and its isotropy and heterogeneity.

Of special importance in pest management is the choice of the pesticide type. Physical and chemical characteristics, toxicity, solubility, persistence, mobility, adsorption, formulation (especially liquid), breakdown products, dynamics of residuals and adverse environmental effects should be evaluated when selecting the type of pesticide to be applied.

Monitoring pesticide occurrence in groundwater is an integral part of pest management. So far only a small number of cases have been reported in literature on groundwater contamination by pesticides. This is not to say that pesticides do not occur in groundwater; the reason is that in the past, and in many regions also today, pesticide contents in groundwater have not been monitored, chiefly because of the high financial and technical requirements involved in their identification at very low concentrations.

Monitoring systems should always be in operation in regions with vegetable, fruit or other intensive agricultural cultivation, particularly when they are irrigated, and in areas with sandy soils and

shallow vulnerable aquifers in which leaching of pesticide into the groundwater system can be expected. Monitoring systems play an important role in groundwater quality preventive protection and are described in more detail in the preceding chapter (6).

A modern approach to pest management is the integrated protection of crops against diseases, weeds and pests. The preventive step in integrated protection entails soil preparation, selection of sowing procedures and rotation of crops, choice of highly resistive kinds of cereals and other crops, use of optimal nitrogen and other fertilizer doses. If a disease, pest or weed has already been identified, farmers should be given a warning signal to prepare pesticides for application in the region, and the kind, time and dose of pesticide and the technique of its application should be recommended with regard to the type of crop. Before the pesticide is applied, evaluation should be made of the recorded data on weeds and diseases in past years, and of qualified forecasts of the potential occurrence and intensity of the disease, pest or weed in question. When selecting a pesticide, priority should be given to those types that do not produce a need for additional chemical treatment; the synergetic effects of pesticide mixtures should be utilized. Biological and biochemical substances or rapidly degradable types of pesticide* should be applied so as to reduce adverse effects on the hydrogeological system.

A licensing policy for new pesticides production should emphasize:

1. selection and testing of pesticides and the dynamics of their residuals; verification of their effects on pests, weeds or diseases and on the crop; toxicological effects on man and animals, including fish; accumulation in the food chain; adverse effects on air, soil and water,

* These include predators (Coccinellidae, Heterobiidae, Chrysopidae), parasites, feromones, hormone stimulators, degradable insecticides, chemical sterilization or sterilization by radiation.

2. licensing conditions for the production and sale of pesticides based on evaluation preceding tests, drafting standpoints of competent authorities, preparing a proposal for approval of their use in agriculture (amount, concentration, time of application, etc.) and including the pesticide in a list of permitted substances for a limited period of time.

3. inspection of the quality of pesticide production in terms of the approved licence; method of pesticide storage and distribution; supervision of farmers to see whether the pesticide is applied in accordance with approved conditions; inspection of crops before sale to consumers to preclude any negative effects on human health, particularly in horticulture and agriculture producing vegetables or fruit.

7.5. IMPACT OF GROUNDWATER CONTAMINATED WITH PESTICIDES AND FERTILIZERS ON HUMAN HEALTH

The physical, chemical and biological composition of groundwater may have positive as well as negative effects on human health. Entry of water polluted with various substances into a hydrogeological system through anthropomorphic activities may be the cause of alimentary diseases, which can grow to epidemic proportions, with potentially fatal consequences.

In this respect groundwater is of particular importance, as it accounts for nearly 100 per cent of water supply sources for populations of developing countries.

In advanced industrial countries, as, for instance, in Europe, groundwater usually provides more than 50 per cent of drinking water. Due to its mobility and ability to transport, transform and absorb pollutants, groundwater is becoming one of the most potentially dangerous contaminating media. It has been reported that in developing countries, polluted water may cause 80 per cent of diseases.

One of the aspects that should be monitored in agro-hydrological management systems is the health risk posed by fertilizers and pesticides via the food chain. By comparison with surface water, groundwater's self-purification potential is markedly lower and lessens with the aquifer's depth depending on the declining amount of dissolved oxygen. In spite of that, contact between groundwater and rock, above all sediments with great ion-exchange potential, may cause in space and time distinct changes in their physical and chemical composition, and biodegradation and microbial activity. In areas under intensive agricultural production and with shallow and vulnerable aquifers, a gradual groundwater quality deterioration is observed. The water often does not meet drinking standard, and adverse effects on human health are known.

Environmental side effects of fertilizers and pesticides, and their absorption into the food chain may occur through the following processes:

1. surface water - crop - man
2. soil - groundwater - man
3. soil - crop - vegetarian food - man
4. soil - crop - animal food - animal - man

The use of inorganic fertilizers and various types of pesticides, and their adverse effect on environment and human health have been rapidly growing from the beginning of this century. At first, pests were fought by salts of arsenic, mercury, copper and zinc, as well as sulphur and barium chloride; later dinitro-compounds, triocyanates and, most importantly, chlorinated hydrocarbons, especially DDT, HCH and its isomeres lindane, aldrin, dieldrin and heptachlor have been introduced. Even low concentrations of the above substances are detrimental to the environment, and chronically toxic. The use of most chlorinated hydrocarbons in farming has now been stopped; however, their residuals in groundwater persist, and have been identified locally and regionally in concentration of 0.001 mg/l and higher, with polychlorinated biphenyls (PCB) occurring in up to milligram concentration.

After 1945, an "explosion" began in farming in the use of organic substances. A broad spectrum of organic compounds is observed in most natural waters. Man takes in organic compounds chiefly through food. So far, they have been appearing in groundwater in harmful concentrations only locally, in some aquifers beneath arable land. Organic compounds of phosphorus pose a risk through their acute toxicity; organic fungicides are a potential source of poisoning and, due to their persistence in soil, cause long-term degradation of the bio and hydrosphere; carbamates are toxic substances, potentially carcinogenic (they contain ethylene-thio-ureas) and possess mutagenic and teratogenic properties. Mercurial fungicides are also highly toxic. Triazine, carbamate and similar herbicides pollute water in as low as trace concentrations.

In view of their effects on human health, pesticides should be monitored as to their level of persistence in soil, ecological-toxicological and neurotoxicological effects, penetration into the food chain, and biotransformation (their intermediate products may be more dangerous for man than the original compounds). In view of human risks farming (including crop and cereal conservation after harvesting) should exclude the use of organochlorine pesticides (especially aldrin, dieldrin, chlordan, DDT and HCH), insecticides based on arsenic and lead, and mordants based on organic mercury, because they can cause acute or chronic conditions and pathological processes, and exert retarding effects on generations to come.

With regard to inorganic fertilizers, an incorrect use of nitrogen fertilizers leads to increased levels of nitrate concentrations in groundwater and the food chain. It is estimated that the total dietary intake of nitrates in drinking water is less than 30 per cent. Hepatotoxic and carcinogenic nitrosamines are highly hazardous, since they easily penetrate biological membranes. High doses of fertilizers may result in nitrates not being metabolized with their deposition in plants as ballast. Spinach, carrot, kohlrabi and beet are especially liable to accumulate nitrogen. There is a well-known and close relationship between high nitrate contents in groundwater consumed for drinking and alimentary methaemoglobinaemia, which can be fatal

for infants (through bacterial action nitrates are reduced to nitrites which cause the haemoglobin in blood to change into methaemoglobin, which is unable to transport oxygen).

Methaemoglobinaemia in infancy under European conditions appears only exceptionally, when private dug wells with high nitrate contents are used for water supply. According to WHO, from 1945 some two thousand cases of methaemoglobinaemia have been reported, with a case fatality of about 8 per cent. Adverse health effects (gastric cancer, birth defects, cardiovascular disease, effects on the thyroid gland) as a consequence of long-term consumption of water with high nitrate contents are under study. Health risks can also arise when high nitrate contents are combined with pesticides, or when their residuals form carcinogenic nitrosamines.

Metal contents in groundwater resulting from farming activities should be subject to monitoring because of their toxic effects on the human organism (its liability to genetic damage), and the ability of these compounds to accumulate in the human body due to their long biological half-life. With regard to organic fertilizers, phosphates should be monitored, particularly when the primary raw material for their production comes from North African territories. These fertilizers may contain cadmium compounds which are leached into the root system. The uptake of cadmium by roots depends mainly on the soil pH and the growth stage at which the fertilizer is applied. Cadmium enters the food chain through crops or water. Cadmium contents in cereals on experimental plots exceeded 1 mg/kg of dry matter. The presence of cadmium in crops, soil and groundwater was monitored in many regions under intensive agricultural activity.

In phosphate fertilizers also, lead has been identified, its contents in crops are higher particularly near roads with dense traffic (in cereal stalks lead contents exceeded 9 mg/kg of dry matter). An increased intake of lead results in anaemia, tiredness and irritability. Reports also mention lead's effect on the growth of long bones during development of young organisms.

Fluorides are also commonly present in phosphate fertilizers, and their concentration increases in groundwater in farmed regions. Long-term consumption of groundwater containing more than 2 mg of fluorides per liter causes, particularly in children, dental fluorosis. In up to 1 mg/liter concentrations, fluoride in drinking water reduces solubility of tooth enamel, supports the growth of teeth, and its effect on human health is positive.

High contents of selenium may occur in drainage water if the soil is rich in this element. Human selenium intakes higher than 10 mg/day may cause gastrointestinal upsets, skin discoloration and bad teeth (T.M.Y. Tebbutt, 1983).

Uncontrolled spills of animal wastes and fertilizing with farm manure (above all pig manure) over shallow, vulnerable aquifers can be a source of groundwater bacterial, viral and parasitic groundwater contamination. Health risks are considerable in such areas, particularly from domestic and shallow wells in developing countries. Diseases can grow into epidemics with potential fatal consequences. Intake of water contaminated in this way may lead to alimentary diseases, above all typhoid, paratyphoid and other salmonellosis, enterovirolosis, yersiniosis, schistosomiasis, etc.

Adverse effects of agricultural activities on human health project into the social and economic spheres (sickness and death rates, migration of population, lower working activity, etc.). In managerial schemes for regional agro-hydrosystems, health risks posed by fertilizers and pesticides should therefore be the subject of continuous control and evaluation.

7.6. CONCLUSIONS

To comprehensively analyze agricultural effects on groundwater obviously requires consideration of both physical processes and decision-oriented aspects. There are at least three issues of general interest in this context.

Firstly, there is a general methodological issue concerning problems in analyzing and modelling, such as those of scale as well as risk and uncertainty. Many problems related to how to translate model results from field studies into regional terms, how precisely to incorporate long and short-term effects of pollution and its control, how to more comprehensively deal with uncertainties in the control objectives and alternatives, and in the structures, parameters and input data of the models employed - all these remain unsatisfactorily answered.

Secondly, the physical processes aspect requires attention. A comprehensive evaluation of the spatial and temporal development of agricultural pollution should be carried out by appropriate means of monitoring and modelling the processes (mechanisms, pathways, etc.), relating pollution sources to water resources so as to arrive at a meaningful water quality impact analysis.

Thirdly, the decision aspect together with the implementation of protective measures have to form an integral part of the overall analysis. Planning and socio-economic evaluation of control strategies require analysis of the trade-offs in and between water supply and management, and also agriculture. Moreover, an assessment of the potential or proved impacts of pollution and its control on man, environment, farm yields etc., needs to be made before control measures can be designed for implementation.

More specifically, looking at the nitrate-pesticides problem, the following conclusions can be drawn.

7.6.1. Agricultural sector

There is a need to document the sources of nitrogen compounds within agriculture, under different conditions of farming production (climate, soil type, cropping pattern, fertilizer type, amount, time and techniques of application, etc.). The aim should be to derive cause-

effect relationships between agricultural practices and the generation of nitrogen compounds that leave the agricultural system. In a similar way, the adverse effects of pesticides on the hydrogeological system should be evaluated (kind, properties and amount of pesticides and the techniques of their application, type of vegetation, soil properties, aquifer vulnerability, etc.). Hence, technological changes in farming production should be evaluated in terms of fertilizer and pesticide use, and environmental impacts. Based on this, the policies to be used to encourage better agricultural management practices have to be defined and evaluated in terms of trade-offs between farming production and groundwater pollution control.

7.6.2. Water supply and management

Dealing with the nitrate-pesticide problem in relation to water supply and management requires taking into account all sources of nitrogen (agriculture, industry, households, atmosphere, etc.) as well as all types of nitrogen compounds (organic nitrogen, ammonia, nitrites, nitrates) that contribute to water pollution. Hence, we are dealing with the "nitrogen problem". Because of the diversity of groundwater supply sources (rivers, lakes, reservoirs, shallow or deep aquifers), the nitrogen problem eventually turns into a multiple pollution source-constituent-resource problem. Since it can only be controlled by conjunctive water resources management, adequate attention must be paid to groundwater pollution, which is of the greatest long-term concern.

Any pollution changes in time and space, as well as the total nitrogen balance should be understood, i.e. there is a need to analyze water quality data in different settings to document trends and correlate trends with pollution activities. In the case of pest management, the policy of licensing new pesticides, producing pesticides that degrade rapidly, constant pest and biological control, insect sterilization, plant selection, soil preparation and a comprehensive monitoring system are especially emphasized for forecasting

future groundwater quality changes due to pesticide-micropollutants in time and space.

7.6.3. Impact on human health

Poor management of the agro-hydrological system results in health risks posed by certain kinds of fertilizers and pesticides via the food chain, water included. In the case of groundwater a relatively lower self-purification potential can be expected. In areas under intensive cultivation, groundwater often does not meet drinking water standards and may be the cause of alimentary diseases and epidemics with potentially fatal consequences. Adverse effects of agricultural pollutants are projected into the social and economic spheres. Sickness and death rates, migration of population, lower working capacity, impact on man's mental state - none of these have hitherto been included in figures on economic losses during evaluation of a regional agricultural system's effectiveness. In fact, consequences to health, above all through pesticide-micropollutants in drinking water, may reach enormous dimensions for the present as well as future generations.

The dramatic case histories of groundwater pollution due to agricultural activities, well known in highly advanced countries, should warn those countries which are less developed. Degradation and restoration of a hydrogeological system is always long-term, and much more expensive than applying protective measures. A Government's political, ecological and moral responsibility for the protection of groundwater resources is therefore inescapable.

Establishment of a government Office of Water Protection, formulation and implementation of a national groundwater policy and strategy including technical, institutional and legal instruments based on Water and Environmental legislation are essential measures for groundwater protection from the adverse effects of agricultural activities.

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CASE HISTORIES

CONSEQUENCES OF IRRIGATED AGRICULTURE IN ARID AND SEMI-ARID AREAS ON GROUNDWATER

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ABSTRACT

The Haryana State (Lat 27°39' to 30°55.5'N, Long 74°27.8' to 77°36.5'E) can be divided into two main hydrological zones. One zone lies in the northeastern part, receiving annual rainfall of 500-1000 mm and having good quality groundwater. The other zone lies in the central and south western region of the state, receiving 300-500 mm. annual rainfall and having brackish groundwater. Introduction of canal irrigation in this second zone has led to a rapid rise in the water table. During the period 1974-81, the rise in water table ranged from 0.55 to 4.89 m, whereas in areas having good quality groundwater a fall in the water table ranging from 0.69 to 1.12 m. has been observed. Due to the rapid rise in the water table, in about 23.6 percent of the area of the state the water table was within 3.0 m of ground surface in 1979. Because of the prevailing poor groundwater quality and various agro-climatic conditions, the water table at this depth has the potential to cause soil salinization. In order to maintain the productivity of these lands, control of the rising water table by installation of appropriate drainage systems is, therefore, inevitable. Failing which, irrigation in arid and semi-arid areas will become a curse instead of a blessing.

INTRODUCTION

The Haryana State, lying in the northwest part of India (Lat 27°39' to 30°55.5'N and Long 74°27.8' to 77°36.5'E) can be divided into two main hydrological zones; one in the north eastern part of the state receiving annual rainfall ranging from 500 to 1000 mm, having soils of medium texture with patches of heavy and light soils, with a flat topography except near the adjoining sivalik hills, and with good

quality groundwater shallow and deep tubewells are the main source of irrigation water in this region. The other zone in the central and southwestern parts occupies nearly two-thirds of the area of the state and receives an annual rainfall varying from 300 to 500 mm. The soils in this area are light to medium textured with a considerable area comprised of sand dunes and undulating topography. The groundwater is mostly brackish with pockets of good quality water found here and there. Canal irrigation is the main method of irrigation in this region. Due to scanty and erratic rainfall distribution in this region, having a semi-arid to arid climate, profitable agriculture was not possible and even monsoon season (July to September) crops often failed in the absence of irrigation facilities. These areas can become productive for agricultural purposes provided these are irrigated judiciously and efficiently. Development of irrigation facilities has, therefore, received the highest priority and during the last 13 years the net irrigated area in the state both by canal and tubewells increased from 1.30 to 1.92 million hectares.

1.17 million hectares (80%) lie in arid and semi-arid, i.e. central and southwestern, parts of the state. Introduction of canal irrigation in the brackish groundwater region without providing a drainage system has led to a rapid and continuous rise in the water table. In the northeastern region overpumping due to the availability of and demand for good quality ground water has resulted in a lowering of water table. Both situations are undesirable. In the former situation the land productivity is threatened due to soil salinization, and in the latter one, increased pumping costs and drying up of shallow tubewells have been experienced by farmers.

MATERIAL AND METHODS

The Haryana State comprises 11 districts (Table 1) and seven of these districts (Sirsa, Hissar, Bhiwani, Mahendergarh, Rohtak Sonapat and Jind) wholly or partly lie in arid and semi-arid areas having brackish groundwater. The district geographical area and the net irrigated area by canals and tubewells for the year 1979 have been obtained from the statistical Abstract of Haryana 1979-1980 (Table 1). Ground-

water table depth observations have been taken from the files of the Haryana State Minor Irrigation and Tubewell Corporation which recorded this data for each June and October since 1974 from a network of more than 1300 observation wells. This is one observation point per 35 Sq. Km area. Based on these observations a water table depth map and an average annual fluctuation map of water table have been prepared. The total area for different water table depth classes (0-3 3-10 and more than 10 m depth) has also been determined. On the basis of the number of deep tubewells, shallow tubewells, dugwells and pumping facilities, as given in the statistical abstract of Haryana and using the standard norms of annual draft per unit, the groundwater balance has been estimated (Pandit, 1981). Groundwater quality data have been taken from the monograph by Manchanda (1976) and, using a weighted average, the average groundwater quality of each district has been estimated.

RESULTS AND DISCUSSION

Haryana State has a total geographic area of 4.42 million hectares, out of which 3.8 million hectares are under cultivation. The net area irrigated by canals and tubewells in the state are 58 and 42 percent of the net total irrigated area (Table 1). The development of canal and tubewell irrigation is strongly dependent on groundwater quality. As may be observed from table 1, canal irrigation dominates in brackish groundwater regions, and tubewell irrigation dominates in areas where groundwater is of better quality. The estimates of the groundwater balance also (Table 2) show that there is negative balance in Karnal and Kurukshetra due to over pumping, and in Ambala district the recharge nearly equals the effective draft. In these areas there is no scope for installing more tubewells or increasing pumping from the existing tubewells. On the other hand the trend in falling groundwater levels in these districts and Ambala and Gurgaon warrants artificial recharge measures or controlled pumping if the fall in water tables is to be checked. Due to the fall in water table, the farmers of the region who have installed large numbers of shallow tubewells have had to lower their pump intakes and in many

Table 1. District Geographical and Irrigated Areas, Annual Rainfall, Number of shallow and Deep Tubewells.

DISTRICT	GEOGRAPH- ICAL AREA (1000 HA)	NET IRRIGATED AREA (1000 HA)		AV. ANNUAL RAIN FALL (CM)	NO. OF SHAL- LOW TUBEWELLS		NO. OF DEEP TUBEWELLS
		CANAL	TUBE- WELLS		DUG WELLS AND PUMPING FACI- LITIES		
Karnal	372	42	189	70	47975	751	
Kurukshetra	373	80	157	75	51037	434	
Ambala	374	5	75	95	21615	775	
Gurgaon	488	31	93	65	34861	188	
Hissar	633	332	31	40	14702	309	
Mahendragarh	298	-	54	55	8829	115	
Rohtak	384	126	54	50	19738	6	
Sonepat	219	56	54	60	14922	44	
Jind	331	140	31	60	11477	85	
Sirsa	427	211	46	32	10292	55	
Bhiwani	509	94	16	35	6374	57	

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Table 2. Districtwise groundwater conditions in Haryana.

DISTRICT	AV. GROUND- WATER QUALITY (MMHOS/CM)	TOTAL		TOTAL EFFECTIVE ANNUAL DRAFT (HA.M)	GROUND- WATER BALANCE (%)	AV. PUMPING (CM/YEAR)	AV. WATER TABEL		AV. CHANGE IN	
		USABLE ANNUAL RECHARGE (HA.M)	DEPTH IN JUNE (M)				1974	1981	1974- 1979	1974- 1981
Karnal	1.99	131876	151243	-14	59	5.12	6.17	8.8	-15	
Kurukshetra	1.34	126308	139149	-10	53	6.81	7.76	3.6	-14	
Ambala	0.69	84272	82494	3	32	7.31	8.43	4.6	-16	
Gurgaon	4.97	120435	76537	36	25	5.31	6.00	18.9	-10	
Hissar	6.30	100651	35523	65	10	13.12	9.77	45.3	-48	
Mahendergarh	3.48	46407	37214	20	19	15.10	13.66	72.7	21	
Rohtak	8.29	58216	35531	39	12	7.94	6.79	43.2	16	
Sonepat	4.60	45277	23361	49	16	4.12	3.55	20.6	8	
Jind	6.44	62032	21882	65	10	13.48	9.11	62.4	62	
Sirsa	5.06	57901	19117	67	7	15.56	11.85	52.0	53	
Bhiani	7.20	47198	6002	88	2.6	27.85	22.96	39.4	69	

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cases farmers experience either reduced discharge or drying of the wells. After two to three below normal rainfall years (1979-1980), this situation becomes very aggravated. The intervening, above normal rainfall years (1976-1978) help in favorably maintaining the groundwater regime. The average annual water table fluctuations for the period (1974-1979) and (1974-1981), given in table 2, clearly show this trend.

With the introduction of canal irrigation in the brackish groundwater regions and limited pumping of groundwater due to quality constraints, a continuous and rapid rise in water tables, has been observed. In considerable areas the water table has already reached a critical depth, posing a threat to land productivity. In a canal irrigated area (Hissar) where the water table remained at less than 3 m depth, the soil salinity has been monitored at a number of locations from 0-150 cm. depth. This data shows an appreciable increase in soil salinity from October 1979 to October 1981 (Table 3). Under the prevailing soil groundwater quality and climatic conditions, the groundwater table at this depth has the potential to cause soil salinization (Talsma 1963, Oswal and Khanna 1978).

Based on groundwater table depth observations from 1974 to 1981, an average annual water table fluctuation map has been prepared indicating areas with magnitudes of annual rise/fall in water table. For each problematic district the percent area under 0-3, 3-10 and more than 10 m water table depth has been estimated. A very appreciable increase, in the size of the area under a 0-3 meter water table depth has been observed (Table 4) from 1974 to 1979. However in 1981, due to 1979 and 1980 being drought years, there was a decrease in the area under this water table depth range, but it was higher than in 1974.

Table 3. E.C. (mmhos/cm) 1:2 saturation extract of Soil from 0-150 cm depth at different locations.

LOCATION no.	OCTOBER 1979	OCTOBER 1980	OCTOBER 1981
1.	0.18	0.19	0.24
2.	0.13	0.25	0.27
3.	0.14	0.15	0.23
4.	1.25	2.04	1.08
5.	0.88	0.84	3.36
6.	0.13	0.24	0.20
7.	0.59	0.93	0.37

In the State as a whole in June 1979 as much as 23.6 percent of the area of the State was within the 3 meter water table depth, which was 9.1 and 11.4 percent in June 1974 and 1981 respectively. In June 1981, about 53.40 percent of the area of the State was within the 3-10 m water table depth. Due to the unchecked rise in water table, the areas presently under the 3 to 10 m water table depth are likely to reach a critical depth of less than 3 m in the next 5 to 10 years if measures to arrest the rise in the water table are not adopted. Contrary to expectations, the rise in water table due to recharge from good quality irrigation water and from rain water has not been accompanied by a corresponding improvement in the quality of ground-water as seen from the data reported in table 5. This is attributed to the presence of large quantities of soluble salts in the soil profile (Table 3), and insignificant underground flow of good quality water from the northeastern parts of the State into the central and western parts due to low transmissivity of the intervening geologic formations. The rapid rate of rise of the brackish groundwater table can be reduced to a considerable extent by lining the entire irrigation water conveyance system and improving field water application efficiency. The detailed water balance studies carried out in these problem areas (Agarwal et al. 1979) showed that, even after the maximum possible improvement in the irrigation system, the rise in the water table will still take place. Therefore, to prevent the

water table rise completely, extraction of a minimum of 8-15 cm of brackish groundwater per year is inevitable. The disposal of this brackish drainage water is highly problematical due to absence of natural drainage courses in the area. A study from Pakistan (ILRI Annual report 1980) shows that because of a rising water table, the area under cotton in the Punjab has decreased from 56 percent to 33 percent of Kharif area. This was mainly due to a reduction in yields caused by high water table conditions. In areas where the water table

Table 4. Percent area under different water table depths in problematic regions of the State

DISTRICT	0-3 m			3-10 m		
	1974	1979	1981	1974	1979	1981
Hissar	2.3	18.8	3.8	44.4	45.9	51.1
Sirsa	1.9	21.9	13.9	34.3	36.3	29.5
Rohtak	11.3	45.2	15.6	51.0	75.4	71.7
Sonepat	18.8	60.9	43.5	66.7	39.5	56.0
Jind	9.2	28.5	14.6	43.9	58.5	55.4

is within 150 cm, the cotton area is only 3 percent of the Kharif area. Where the water table is at 3-5 m the cotton area is about 5 percent less than in the 5 m zone. In another area on Dadu Canal in Sind, cotton occupied 44 percent of the Kharif area in 1937-1938 and by 1967 it was reduced to 2 percent as a result of a high water table. Similarly in Hansi Tehsil of the Hissar district and Kaithal (Karnal), cotton was the major monsoon season crop, but now the cotton has been replaced by rice due to high water table conditions. Therefore, in order to prevent the spread of high water table and salinity conditions to other areas of Haryana and Punjab and to maintain the productivity of lands, checking the water table rise and also its lowering to below 3 m by installing appropriate drainage systems is most urgently required. In conclusion it can be stated that introduction of canal irrigation in arid and semi-arid areas without adequate drainage systems becomes a curse instead of a blessing.

Table 5. E.C. (Electrical Conductance) of groundwater samples of some location, Hissar (1969-1978); mmhos/cm

DATE		SITE 1	SITE 2	SITE 3	SITE 4
December	1969	3.48	4.80	14.40	0.96
January	1970	3.54	5.56	16.20	1.56
January	1971	2.88	4.80	15.80	0.90
January	1972	1.80	4.50	12.03	1.20
March	1973	3.78	6.60	20.52	3.54
July	1974	3.66	6.90	18.60	1.20
February	1975	2.10	4.26	12.90	0.78
February	1976	4.26	8.15	24.20	1.94
January	1977	2.92	9.10	9.45	2.53
May	1978	2.36	5.09	14.67	2.77

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IMPACT OF AGRICULTURE ON GROUNDWATER IN IRELAND

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ABSTRACT

Ireland has large water resources. Only 5.3% of developable waters are as yet developed, to supply some 650 lit/day/capita to the population of some 3.37 million people. State of development varies in each of the seven water resources regions.

Precipitation is fairly evenly distributed over the year, but the percentage infiltrating to form groundwater varies quite sharply. Some 61% of infiltration occurs in the four winter months November to February, when agricultural activities are low. Only 10% infiltrates in the four summer months, May to August, when agricultural activities are high. In all, annual groundwater amounts to some 24.8 km³, of which 50% is considered to be recoverable. Capital groundwater reserves must be large, but are unquantified.

Under these conditions, the impact of agriculture on groundwater quantities is negligible. Of the annual extraction of some 170x10⁶ m³ of groundwater, some 66x10⁶ m³/year are used in different agricultural activities. Drainage operations however have effects on Irish groundwater. Such lands may overlie impermeable strata or pans, or may receive concealed or visible groundwater discharge. Their drainage will affect the groundwater in various ways.

There has been a considerable impact of agriculture on groundwater quality. The effects on the atmosphere and on precipitation are not identifiable. Effects of diffuse infiltration are treated with respect to: (i) application of ground limestone (lime); (ii) applica-

tion of K.N.P. inorganic fertilizer; (iii) spreading of organic slurries; (iv) development of organic nitrogen in soils, mainly after ploughing of grasslands; and (v) residues from herbicides, fungicides and pesticides. The infiltration of these substances spread on the land is closely related to the interaction between times of groundwater recharge and times of fertilizer application; this is emphasized in table 1.

Effects of concentrated infiltration are treated under seven sub-heads. (i) Infiltration of polluted surface waters; (ii) localized farm infiltration; (iii) concentrated waste disposal from feedlots; (iv) concentrated waste disposal from silage; (v) concentrated waste disposal from agro-industries; (vi) disposal through sinkholes and quarries; and disposal by deep well injection. These operations are deliberate, and not related to times of groundwater recharge. They are often into the limestone aquifers, and so doubly dangerous.

INTRODUCTION

Quality of Groundwater

While at times and local places, some contamination of Irish groundwater has and does occur, in general the groundwaters are little polluted by agriculture or other human activities. In considering the composition and quality of groundwater, precipitation, the source of the water, is first noted; then surface waters which may infiltrate; and then the groundwater as it is known today.

Irish precipitation is of oceanic origin. Chloride ion content can be high close to the coast; over the 10-year period 1971-80, Valencia averaged 21.3 ppm Cl^- , with peaks of 57 and 37 ppm in December and January; this gives a concept of background chlorine in coastal areas, as Aldwell & Wright, 1978. The NO_3 -N range in Irish precipitation is small, in the 0.2 to 0.6 ppm range (Mathews & McCaffery, 1977). The SO_4 lies in the 2 to 7 ppm range. Tritium has been recorded at Valencia since 1952, and can be used in groundwater investigations in Ireland (Bowen & Williams, 1972). Acid rain, indicated by sharp falls

in the pH, has but the slightest effect in Ireland, being confined to the east coast, as in Mathews, McCaffery and Hart (1981).

Evapotranspiration can increase the original Cl , NO_3 and SO_4 in the precipitation, as it changes from surface to underground water. Burdon and Cullen (1980) found that in the Caradocian volcanic aquifer of south-east Ireland, the Cl content increased from some 9 ppm in precipitation to 25 ppm in the groundwater; there was no other source of chloride ion.

Infiltration of polluted surface water can, of course, pollute the groundwater. A survey of some 2.900 km of Irish rivers in 1979 showed that 6% of the total length was seriously polluted, there was moderate pollution over 22% of the total length, while 72% was in satisfactory condition (McCumiskey, 1981). Lakes present more of a problem. The 1973 national survey indicated 13 lakes which were excessively or moderately eutrophic, located mainly in the inland counties of Cavan, Westmeath, Longford and Monaghan. Since then, there has been an improvement, with Lough Sheelin excessively eutrophic on occasions due to piggery waste, (McCumiskey, 1981, p.8-9).

The 1979 Survey report (Daly, March, 1979) summarizes the 123 most reliable groundwater analyses made by the Survey over the preceding four years. In general, the $\text{NH}_3\text{-N}$ (saline and free ammonia) was less than 0.05 ppm, with an abnormal high of 0.14 ppm in some groundwaters from the Clay Gall and Swan Sandstone aquifers of the Castlecomer area. For nitrate, $\text{NO}_3\text{-N}$, 67% showed less than 3.0 ppm; the highest reported was 4.7 ppm from the ORS aquifer in Co. Waterford. A recent (1981) survey of groundwaters from limestone aquifers in Co. Sligo confirm the generally uncontaminated nature of groundwater in Ireland.

IMPACT OF AGRICULTURE ON GROUNDWATER QUANTITY

Ireland has developable water resources estimated roughly at 22,800 million cubic meters per year; of this, 10,400 million would be from overland flow and 12,400 million from underground sources. Current extraction amounts to some 1,066 million cubic meters per year, or 5.3% of potential. Current extraction is made up of $363 \times 10^6 \text{ m}^3$ by

public bodies, $249 \times 10^6 \text{ m}^3$ for industry, $27 \times 10^6 \text{ m}^3$ for cooling of thermal power plants, $130 \times 10^6 \text{ m}^3$ for agricultural purposes, and $48 \times 10^6 \text{ m}^3$ for rural domestic water supplies. With a population of 3.37 million, this gives an overall water supply of 870 lit/day/capita, or excluding thermal cooling water (most of which is returned to rivers), 645 lit/day/capita.

Quantity of Groundwater Used for Agricultural Purposes

Total groundwater extraction is estimated at $169 \times 10^6 \text{ m}^3$ per year, or 16% of overall water extraction. Public bodies extract $60 \times 10^6 \text{ m}^3$, industry extracts $63 \times 10^6 \text{ m}^3$, while rural domestic supplies are very much dependant, and extract $46 \times 10^6 \text{ m}^3$ for that purpose.

The amounts of these groundwater extractions which are used in agriculture can only be estimated in a general manner. Agricultural purposes include: domestic supplies (including dairy, washing, etc) for rural dwellings and farmyards, and also for small villages; supplies for agro-industries; water for stock, horticulture; related uses. There is virtually no irrigation in Ireland. Based on these considerations the overall use of groundwater for agriculture totals some $66 \times 10^6 \text{ m}^3/\text{year}$, obtained from the following sources:

From public bodies	+ 10% of 60 =	$6.4 \times 10^6 \text{ m}^3/\text{year}$
From industrial extractions	+ 20% of 63 =	$13.6 \times 10^6 \text{ m}^3/\text{year}$
For rural domestic supplies	all of 46 =	$46.0 \times 10^6 \text{ m}^3/\text{year}$
Total volume of groundwater	=	<u>$66.0 \times 10^6 \text{ m}^3/\text{year}$</u>

This amount of groundwater represents but a little over 0.5% of the annual replenishment of the recoverable groundwater (12.4 km^3) in Ireland. While there may be significant regional or local variations, the overall average is so low that in Ireland the quantity of groundwater used for agriculture is negligible in relation to annual replenishment.

Impact of Drainage Operations on Groundwater Quantity

Drainage operations are a major means of increasing the amount and of improving the quality of land available for intensive agriculture in Ireland. They vary from major arterial drainage schemes embracing a whole river basin, through such operations as draining fens and bogs, both raised and blanket, by State enterprises (Bord na Mona, ESB, Forestry Commission) to works undertaken by individual farmers.

One aspect of such works affect groundwater, and is so considered here. Lands calling from drainage may overlie impermeable rocks or cover; or they may be located over and below areas of groundwater seepage or springs. The two cases are very different, though in some schemes this difference has not been taken into consideration. For several years, the Agricultural Research Institute has been studying relationships between soil, geology and drainage problems; the most recent report (Mulqueen & Gleeson, 1981) has been used to help prepare the following observations.

Four main conditions lead to impermeability and water-logging due to non-infiltration of precipitation and runoff. (i) Outcrops of impermeable rock, often overlain by thin soils or blanket mountain bog, give rise to conditions calling for drainage; such occur at Griggins Bridge in Galway where there are Silurian sandstones; likewise at Gallarus Oratory, Co. Kerry, where the Dingle Beds outcrop. The drainage of such soils has little effect on groundwater. (ii) Lacustrine marls, deposited in lakes of the late glacial period, and subsequently invaded by vegetation and often converted to raised bogs. Their drainage has little effect on groundwater conditions. (iii) Impervious layers develop in some soils, some associated with Namurian shales, others with drumlins and a third group associated with Old Red Sandstone (ORS) outcrops. Their drainage problems are set out by Mulqueen (1974). Their drainage can increase infiltration, since they usually lie sandwiched in between permeable soils. (iv) Impermeable pans, iron, silica and calcrete, are not uncommon in Ireland. Iron pans develop in soils derived from shale, sandstone, granites and metamorphics (as Crompton, 1956). Iron and silica pans

often occur together; but silica pans can occur on their own. Calcrete pans are also common, and were noted in many places as long ago as 1907 (Kilroe). These pans tend to occur at the base of the vadose zone, where conditions change, as from reducing to oxidizing, from confined to free, etc. Hence the drainage (and breakup) of such pans can increase groundwater movement. It may also affect groundwater chemistry, in particular with respect to precipitation of iron and manganese, well-known causes of trouble in domestic water supplies.

Groundwater discharges giving rise to fens and marshes can be considered under three headings, again following data from Mulqueen & Gleeson, (1981). such groundwater discharges tend to occur on low ground, and so tend to form part of arterial drainage schemes. The concept of intercepting the groundwater above the zone of seepage-springs has not been applied in Ireland.

(i) Groundwater discharges from bogs are usually seepages, as Dooge reported, (1975). These waters are acid. Since peat generally overlies impermeable ground, drainage is unlikely to affect groundwater discharge; but the change from acid peatland water to less acid may affect the hydrochemistry of the area.

(ii) Groundwater discharging from Quaternary sands and gravels give rise to many situations regarding drainage; in many cases the discharging water is ascendant, under some confining pressure. Mulqueen & Gleeson quote examples from the Galtrim moraine at Kilcorney, Enfield, Co.Meath; this is an area of warm springs, whose Quaternary geology has been researched by Synge (1950). Effective drainage operations require a full understanding of the hydrogeology of the affected area.

(iii) Terminal moranic conditions have been identified as giving rise to many conditions calling for drainage. These are very common along the moraine marking the southern termination of the second or Midlandian ice-sheet. Local glaciations in the Wicklow and Kerry mountains gave rise to similar terminal moraines, now often associated with drainage problems. Such drainage will normally result in more rapid groundwater discharge; groundwater extraction for other purposes might reduce groundwater levels in aquifers and dry-up seepages and the resulting marshes.

Future Availability of Groundwater for Agriculture

The quantity of groundwater available for future use in agriculture and agro-industries is practically unlimited. Use of 10% of recoverable annual recharge would supply $1,242 \times 10^6 \text{ m}^3$ of good groundwater, compared with $66 \times 10^6 \text{ m}^3$ now used annually in agriculture.

Attention is drawn to the thermal qualities of groundwater. Warm springs occur in Ireland, and are now under investigation (Aldwell & Burdon, 1980). They offer a potential for horticulture and carp ponds. Likewise heat pumps extracting energy from normal cold (9.5° to 10.5°C) can be utilized to warm water for use in swimming pools, such as that are now in operation at Tuam.

IMPACT OF AGRICULTURE ON GROUNDWATER QUALITY

Too often, the impact of agriculture on groundwater is considered only with regard to pollution - actual or potential - from wastes of different types. In this presentation, a balance has been held between all the impacts of agriculture on groundwater - desirable and undesirable; nevertheless, the impact of modernizing agriculture on groundwater is connected with actual or potential pollution of this groundwater.

There has been a major intensification in farming before and since Ireland's accession to the EEC. Those aspects related to increased use of fertilizers and to silage making are best summarized as follows:

N fertilizer	from	5,000 tons in 1948	to	47,750 in 1966
N fertilizer	from	47,750 tons in 1966	to	275,000 in 1981
P fertilizer	from	56,083 tons in 1966	to	63,000 in 1980
K fertilizer	from	93,065 tons in 1966	to	147,000 in 1980
CaCO_3 (lime)	from	1.01 million in 1962	to	1.7 million in 1972
Silage made	from	3 million tons in 1969	to	12 million in 1979

The inputs of these fertilizers, together with organic nitrogen, from decay of vegetation and from slurry spreading, as well as residues from herbicides, fungicides and pesticides may reach the atmosphere and the waters from diffuse applications. Concentrated waste disposal includes farm waste (including dips), waste from feedlots and silage pits, from agro-industries; these may affect groundwater through pollution of infiltrating surface waters, or directly. There can also be point injection through sinkholes and quarries, or by disposal through deep boreholes.

Effects of Agriculture on Precipitation

The available data indicates that there has been slight to nil pollution of Irish precipitation due to agriculture, or indeed to other causes. The acid rain of several regions of the world, leaching increased amounts of Ca, K and even Al from the soil (as Likens, 1979), has not been identified in Ireland, except possibly in parts of the East and South-East, (Mathews *et al*, 1981). However, from research at Johnston Castle, (Kiely, 1981) reports a loss as gas of high percentages of the nitrogen in pig and cattle slurry spread as a fertilizer. Biogas from animal waste is not used as a source of energy on any appreciable extent in Ireland; it escapes to the atmosphere.

Effects of Agriculture in Zones of Diffuse Infiltration

Zone of diffuse infiltration are those areas where infiltration occurs more or less directly from the precipitation falling on them, without any concentration of the water by overland flow and runoff to form streams, rivers and lakes. In Ireland, such infiltration is normally through a cover of Quaternary drift, of varying thicknesses; such underlies almost all land used for intensified agriculture. This cover will act to retard infiltration and can retain most if not all of applied chemicals.

Of most importance still is the fact that most fertilizers and slurries are applied at times when groundwater infiltration is low. Table 1 is designed to emphasize this fact. During the four winter

months from November to February, some 61% of groundwater recharge takes place; during that time the only large fertilizer application is P&K in large amounts to grass, plus some nitrogen to grass also. On the other hand, most fertilizers and much lime are applied during the four spring-summer months from March to June when infiltration to groundwater is small, only some 16% of the annual total. Winter cereals call for P&K in autumn, when groundwater recharges again becomes important; this is a period where P&K residues may leach to groundwater.

The effects in zones of diffuse infiltration may be considered under five subheadings, dealing with: lime; N.P.K. fertilizers; slurry spreading; organic nitrogen; and herbicides, fungicides and pesticides.

(i) Lime. Application of burnt lime and now of crushed or ground limestone is traditional in Irish agriculture. It is used to replace lime leached from the soil and utilized by plant-animal uptake. It lowers the pH, and makes infiltrating groundwater less aggressive against the carbonate aquifers. These tend to have a pH in the 7.2 to 7.5 range, with TDS in the 380 to 480 ppm of TDS (as Daly, 1979). The application of lime has thus no deleterious effect on Irish groundwaters.

(ii) N.P.K. Fertilizers. These fertilizers are applied only to the 42,300 km² under hay, silage and pastures, and to the 4,550 km² under corn, roots and green crops, as in 1979. Taking the detailed county returns for fertilizer use in 1979, the hay-silage-pastures received 226,287 tonnes of N, 55,315 tonnes P and 130,139 tonnes K; the corn-roots-green crops received 32,890 tonnes N, 19,040 tonnes P and 42,354 tonnes K. If this had been spread evenly over the total areas under these crops (which is not the case), and if 10% were leached into the groundwater, then the groundwater under these areas could have contained the following:

N = 2.0, P = 1.2 and K = 2.6 ppm under the corn, roots, etc. area.
N = 1.5, P = 0.4 and K = 0.8 ppm under the hay-silage, etc. area.

Since these groundwaters would be diluted by groundwater from outside the fertilized areas, and since leaching of 10 % of applied fertilizers would be on the high side, these figures are upper limits to what might be expected in Irish groundwaters from N.P.K. fertilizers. On the other hand, more concentrated applications are usual over smaller areas; in such cases, local N, K and P may be higher in a limited area of groundwater, but liable to appreciable dilution with unaffected groundwater from neighboring areas.

(iii) Slurry Spreading. Pig and cattle slurries are being spread at increasing rates on Irish farms. This is done in the summer months, when soil moisture is below field capacity; oxygen must be available, and there is a coefficient of mineralization.

From field investigations over three years at Hoarstone (450 mm infiltration per year) and at Castlebridge (300 mm infiltration per year), Sherwood (1981) found that when pig slurry is applied at 400 kg/ha/yr, the resulting concentrations of $\text{NO}_3\text{-N}$ in soil moisture at a depth of 1 meter was 4 ppm for Hoarwood, and 1 ppm and 4 ppm at the two Castlebridge plots. Increasing the application to 700 kg/ha/yr increased the corresponding $\text{NO}_3\text{-N}$ to 17, 1 and 10 ppm; higher applications gave 36, 1.5 and 32 ppm. On the control plot (no slurry) the corresponding $\text{NO}_3\text{-N}$ figures were 0.8, 0.6 and 1.7 ppm. It is clear that slurry can give rise to higher nitrates in groundwater than can N fertilizer.

A study of surface runoff from six other plots at Hoarstone and Castlebridge are of direct interest, (Sherwood & Fanning, 1981). The findings are complex, but in general $\text{NH}_4\text{-N}$ fell off rapidly changing to NO_3 and to gaseous nitrogen; BOD fell off rapidly; $\text{PO}_4\text{-P}$ tended to remain at 30 ppm for some time, but did not exceed this figure. Such runoff water could of course infiltrate to form groundwater elsewhere.

(iv) Organic Nitrogen. Research has shown that leaching of N from fertilizer applications is negligible up to applications of 240 kg/ha/year. However, when grasslands are ploughed, there is a large release of soil nitrogen for the first four or five years. Release of soil N is about 200 kg/ha in the first year, 100 kg/ha in the second year, and then some 40 kg/year. This soil nitrogen mineralizes throughout the winter since soil temperatures in Ireland seldom fall below 5°C. This is the time of groundwater recharge, so there is considerable leaching of soil nitrogen, say from 20-70 kgN/ha/year, or an average of about 35 kgN/ha/year. With infiltration of 363mm/year (Irish average), then the groundwater under such areas would contain from 6 to 20 ppm of N.

(v) Herbicides, fungicides and Pesticides. Chemical weed control has expanded rapidly in Ireland; thus none of the sugarbeet acreage was treated with herbicides in 1960, while some 98% was sprayed in 1970. Many herbicides are used, and this variation reduces the danger of a buildup of harmful residues. Fungicides are used, expanding from those for potato blight to many for disease control on cereals. Insecticides are not used on grass, but to some extent on cereals and on potatoes (say 40,000 ha), as in Robinson (1982). Residues from these herbicides, fungicides and pesticides were sufficient to affect the top of the food chain for birds-of-prey; the peregrine falcon declined from some 200 to 15 breeding pairs in the 1960; better control has enabled this bird to regain its breeding position in the 1970s.

As yet, there are no signs of harmful effects in groundwater, though it is likely that such insecticides as the organochlorides may have entered groundwater in small, but undetected, amounts.

Effects of Agriculture from Concentrated Infiltration.

Concentrated infiltration usually represents a definite operation to get rid of waste by allowing it, or forcing it, into the underground, and so normally into the groundwater which occupies the subsurface voids. Such concentrated infiltration is normally more easily achieved

ved, and produces the most serious contamination over long distances, in fissured and sometimes karstified aquifers, such as the main Carboniferous aquifer underlying most of the central areas of Ireland. The Quaternary cover may produce some filtration, but it is often thin or missing around farmyards built on or near rock outcrops, or around quarries.

The effects of concentrated infiltration of waste from farming operations in Ireland may be summarized here under some seven subheadings: from polluted surface waters; localized farm infiltration; from feedlots; from silage; from agro-industries; through sinkholes and quarries; by deepwell injection.

(1) Infiltration of Polluted Surface Waters. Where outcrops of aquifers underlie streams, rivers or lakes, there will be movement of water, infiltration when groundwater levels are less than surface water levels, and discharge of groundwater when relative levels are reversed. Thus a brief note is required here on pollution of surface waters by agricultural activities.

Pollution of surface waters is more obvious than pollution of groundwater. Such pollution has been studied by An Foras Forbartha (as Toner & Lennox, 1980), a & b; McCumiskey, 1981); there have been several prosecutions under the 1977 Act. In certain areas, including Cos. Cavan and Monaghan, intensive pig and poultry production has led to serious pollution of surface waters, in particular the many lakes of that region of Ireland. A groundwater survey of these counties found that "The level of nitrates and sulphates (in groundwater) in the Lough Sheelin area of Co.Cavan have been found to be higher than the levels prevailing in the rest of that region: (An Foras Forbartha + Geological Survey, Vol.1, p.31).

Toner & Lennox (1980) selected seven sites on major rivers far from possibilities of urban or industrial pollution. From the 1972-73 period, with minima all less than 1.0 ppm N and a maximum of 3.4 ppm N at Milford Bridge on the Barrow, nitrate levels all increased, with

the maximum again at Milford Bridge, with 5.8 ppm N in the 1978-79 period. "A study of Nitrate Levels in the Aquifers of the Barrow River Valley" by E.P. Daly and D. Daly is presented to this Prague Symposium, and gives details of the Barrow Valley, where pollution problems exist, but less from agricultural activities than from urban and industrial wastes.

(ii) Localized Farm Infiltration. Waste from farmyards and other areas of livestock concentration is the most common and widespread source of groundwater pollution. Farm houses, residences and cottages usually discharge domestic waste through septic tanks and cesspits, all providing degrees of water purification. Many rural dwellings are now supplied with piped water (of underground or surface origin) coming from afar. The pollution of the farm well or borehole may occur, but is less likely to have health implications.

The runoff, usually rain-induced, from farm buildings and yards is high in suspended solids, organic content and BOD. It generally contains much faecal bacteria. There may be mineral oil from machinery, chemicals from sheep dips, and related contaminants. UNESCO (1980) estimates that the volume of waste water amounts to some 1,000 m³/head/annum. These volumes of contaminated water usually soak into the ground under the farmyard area, often located on an outcrop or near-outcrop of the rock, usually limestone. A well-drained farmyard was once an asset.

There is clear evidence of pollution of farm wells by such waste water. A detailed study was made of farmyard wells in an area of Galway underlain by limestone. Pollution varied from farm to farm, but almost all wells showed some pollution at one time or another. There was a tendency for pollution to rise sharply after rains, particular those of autumn. Relationships between nitrite and nitrate contamination are complex, and as yet not fully understood, the study is continuing.

(iii) Concentrated Waste Disposal from Feedlots. Intensified farming in the form of feedlots and piggeries has been undertaken by many farming enterprises and individual farmers. These produce large quantities of urine and faecal material; 15 m³/yr for bovines, 3m³/yr for pigs and 5 m³/year per 100 poultry. This material is liquified in various ways, so that annual discharge can range from 10³ to 10⁵m³/yr/feedlot. This material may in part or totally be retained as fertilizer; but since such fertilizer can be spread effectively only in summer-autumn, and the cost of storage is high, much is discharged to soak away into the ground and the aquifers, as with farm waste from less intensive units.

The pollution of surface waters with slurry and other waste from feedlots, piggeries and other intensive units has already been noted. In some cases the agricultural enterprise may own only the actual feedlot and not the surrounding land. In such cases, slurry has to be sold/given to farmers, or else discharges as surface waste, or induced underground through limited soak areas, Clogging is usual.

(iv) Concentrated Waste Disposal from Silage. The amount of silage made in Ireland increased from 3 million to 12 million tons between 1969 and 1979, and is increasing at an accelerated rate. Silage gives rise to an effluent at the rate of some 30³/year/100 tonnes; where fed to cattle, the effluent increases to some 100 to 1,000 m³/yr/animal. The effluent is high in suspended solids, has a BOD in the range of up to 6x10⁴ mg/liter, and it contains carbohydrates, phenols and other organic components as UNESCO (1980, p. 6). While of value as a fertilizer, it is often allowed to soak away into the ground and the aquifers.

Silage effluent is highly acid, and this can have serious effects on the groundwater. In particular, Fe and Mn will be taken into solution and may be reprecipitated as the groundwater becomes less acid and the zone of oxidation is reached. There are strong objections to such iron and manganese staining where such water is used for domestic supplies.

A clear example of contamination by silage and farmyard waste occurred at the springs at Rosses Point Waterworks of Sligo County Council in July, 1980. From information supplied by Mr. N. D. Farrell (letter of 23 Nov., 1981), it is learnt that samples of spring-river water collected on 3/7/80 contained up to 16 ppm of Mn. Using NaCl tracer (half-ton) the point source of pollution was identified as a farm discharging farmyard slurry and silage runoff through a soakpit into the karstified limestone aquifer which underlies that area of Sligo. It took the salt 12 hours to move from the soakpit to the springs. However, another source of water supply had to be brought into use, at considerable cost and loss to the area, which is a well-known beauty spot and summer tourist resort.

(v) Concentrated Waste Disposal from Agro-Industries. Milk and meat processing plants are the most widespread of agro-industries; but there are also four sugarbeet plants, numerous vegetable processing plants, as well as tanneries, breweries and one distillery. Fish processing plants discharge their waste to the sea. Saw mills, peat drying and other such operations lie of the fringe of agro-industries.

As transport and refrigerating have improved, creameries have become larger and fewer. They have much liquid waste, some highly organic. It is usual to hold such waste in ponds, where evaporation can be of help, and dilution by precipitation a hindrance. Offal, blood and other waste from meat processing plants can be highly polluting. Such waste is usually treated before it is discharged, often to rivers. How much goes directly to groundwater is not known, but such installations are clearly possible point sources of groundwater pollution. Many agro-industries are located in or close to towns; their waste can be treated in the municipal sewage system.

(vi) Disposal through Sinkholes and Quarries. This form of waste disposal is used by many, but is particularly tempting to rural dwellers. Sinkholes or related collapse structures leading into karstified systems of underground caves and joints are common on many

farms overlying limestone formations. Traditionally, they were used for waste disposal; many have been filled. Disused quarries fall into the same category. With increasing amounts of liquid waste from intensified farming it is very tempting for the farmer to discharge more and more into the old sinkhole or quarry he has used in the past.

Thus, writing on the extensive cave-system of North-West Clare, Tratman (1969, p.291) states "Natural holes in the ground are both a worry and a Godsend to the farmer. Cattle and other beasts may fall down them and be killed. Likewise, dead beasts may be disposed of by throwing them into such holes and the explorer (speleologist) is sometimes unlucky in finding one or more in a ripe state... A swallet may even be used as the disposal site for offal from the local slaughterhouse".

(vii) Disposal through Deep Well Injection. This mode of waste disposal has not, as far as is known, been used in Ireland. We have little information on the deep aquifers of Ireland. Some may be saline, sealed and a good place for waste disposal.

Table 1. Temporal relationships between rates of infiltration to groundwater and the application of fertilizers to different crops; when groundwater recharge is large, fertilizer application is small.

TWO-MONTH PERIODS		N + D	J + F	M + A	M + J	J + A	S + O	TOTALS
PRECIPITATION								
Markee Castle, 1931-60	mm	239	187	133	152	2203	217	1131
% of Annual		21.2%	16.5%	11.7%	13.4%	18.0%	19.2%	100%
WATER MOVEMENT								
Evaporation.....mm		20	20	60	135	160	82	477
Surface Runoff.....mm		100	65	25	5	20	79	294
Infiltration to GW.....mm		119	102	48	12	23	56	360
Evaporation.....%		1.8%	1.7%	5.3	11.9	14.2	7.3%	42.2%
Surface Runoff.....%		8.9%	5.8%	2.1%	0.4%	1.8%	7.0%	26.0%
Infiltration to GW.....%		10.5%	9.0%	4.3%	1.1%	2.0%	4.9%	31.8%
GROUNDWATER RECHARGE.....%		33.0%	28.3%	13.5%	3.5%	6.3%	15.4%	100%
TIMING OF FERTILIZER APPLICATIONS -								
Rough Percentages								
Ground Limestone								
On cereals.....%		-	-	60%	20%	-	20%	
On grass.....%		-	20%	20%	20%	20%	20%	
N Fertilizer								
On cereals.....%		-	-	50%	30%	-	20%	
On grass.....%		-	20%	40%	30%	10%	-	
On root crops.....%		-	-	50%	50%	-	-	
P&K Fertilizers								
On cereals.....%		-	-	70%	10%	-	20%	
On grass.....%		20%	50%	20%	10%	-	-	
On root crops.....%		-	-	60%	40%	-	-	
Slurries, organic								
On grass.....%		-	-	40%	50%	10%	-	

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ELEVATED LEVELS OF NITRATE IN GROUND WATER BENEATH INTENSIVELY GRAZED PASTURELAND IN NEW ZEALAND

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ABSTRACT

Lowland plains are important regions of intensive pastoral agriculture in New Zealand. Agricultural production in some areas is being increased by irrigation. The potential exists for contamination of alluvial aquifers, located beneath the plains, by nitrate leached from pastureland. Nitrate-N concentrations in parts of several alluvial aquifers already exceed 10 g m^{-3} and range up to 60 g m^{-3} . Concentrations vary considerably between summer and winter in response to changes in the volume of drainage entering ground water.

Urine deposited by grazing stock is the principal source of nitrate leached from pasture. Nitrogen is applied in urine spots at a rate equivalent to 500 kg ha^{-1} . Field measurements indicate leaching of $10\text{--}25 \text{ kg N ha}^{-1}$ annually from non-irrigated pasture and $65\text{--}70 \text{ kg N ha}^{-1}$ from surface-irrigated pasture. Although a seasonal pattern of nitrate concentrations is retained in the unsaturated alluvium above the aquifers, the seasonal concentration trend observed in ground water results almost exclusively from temporal variation in the volume of drainage entering ground water.

Mass balances of the major nitrogen inputs and outputs for grazed pastureland confirm the measured leaching losses. Approximately 15 and 23 percent of the nitrogen excreted by grazing sheep is estimated to be leached from non-irrigated and surface-irrigated pastures, respectively.

INTRODUCTION

The principal aquifers of New Zealand are located in unconsolidated alluvial sediments that form lowland coastal plains. The plains are also important areas of intensive pastoral farming. The shallow, well-drained soil cover of the plains makes the underlying ground water particularly vulnerable to contamination originating at the land surface. Concern has been expressed recently at the apparently widespread occurrence of high nitrate concentrations in the alluvial aquifers. Fears are also held that continued intensification of pastoral agriculture by surface irrigation may significantly increase the present levels of nitrate in ground water.

The purpose of this paper is to describe the occurrence and source of nitrate in the alluvial aquifers and to illustrate the quantities of nitrate leached from non-irrigated and surface irrigated pastures on the lowland plains.

NITRATE CONCENTRATIONS IN GROUNDWATER

High concentrations of nitrate have been observed in all but one of the major alluvial aquifers in New Zealand (Burden, 1982). In most regions intensively grazed pastureland was identified as the principal source of nitrate. Detailed studies have been conducted on three lowland plains.

Nitrate contamination of New Zealand ground water was first recorded in the Waikato Basin (Baber and Wilson, 1972). Out of a total of 87 sampled wells, nitrate-N concentrations in 28 (32 percent) exceeded 10 g m^{-3} with a maximum of 60 g m^{-3} . The highest concentrations were thought to occur in shallow perched aquifers. The mid-Canterbury Plains are underlain by a single water-table aquifer that is quite uniformly contaminated by nitrate (Quin and Burden, 1979).

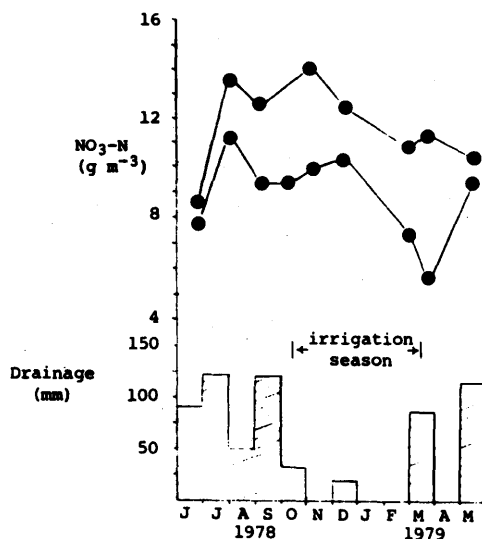


Fig. 1: Seasonal Variation in nitrate-N concentration in mid-Canterbury wells and monthly estimates of subsurface drainage

Away from regions affected by river recharge, nitrate-N concentrations measured near the water table (<20 m) were generally in the range $8\text{--}15\text{ g m}^{-3}$. Nitrate contamination persisted to greater depth beneath a community surface-irrigation scheme and concentrations were higher than beneath non-irrigated pasture.

Beneath a part of the Heretaunga Plains, nitrate concentrations near the water table exceeded 10 g m^{-3} and ranged up to 57 g m^{-3} (Burden, 1980). Concentrations varied by as much as 100 percent between summer and winter (Fig. 1). Significantly lower concentrations, generally less than 2 g m^{-3} , were recorded near zones of river recharge and in confined aquifers.

SOURCE OF NITRATE

In many developed countries high concentrations of nitrate have almost exclusively been attributed to the excessive application of nitrogenous fertilizer to agricultural land. In New Zealand, however, virtually no nitrogen fertilizer is applied to pasture; soil fertility is instead maintained by fixation of atmospheric nitrogen by clover. Although nitrogen is fixed in a grass/clover pasture system at an annual rate of 100–300 kg ha⁻¹ (Hoglund et al., 1979), this does not necessarily lead to high levels of nitrate in soil and drainage water. Plant uptake of inorganic nitrogen largely keeps pace with the rate of mineralization of soil organic nitrogen. Stock urine, however, is voided in sufficiently concentrated spots, equivalent to approximately 500 kg ha⁻¹ (Doak, 1952), that a pasture is unable to fully utilize the applied nitrogen. The subsequent rapid conversion of urea to nitrate (Quin, 1979) results in appreciable nitrate leaching from urine spots whenever rainfall exceeds soil moisture retention capacity (Quin, 1982). Irrigation may enhance nitrate leaching by permitting stock numbers and the through-flow of water to be increased significantly.

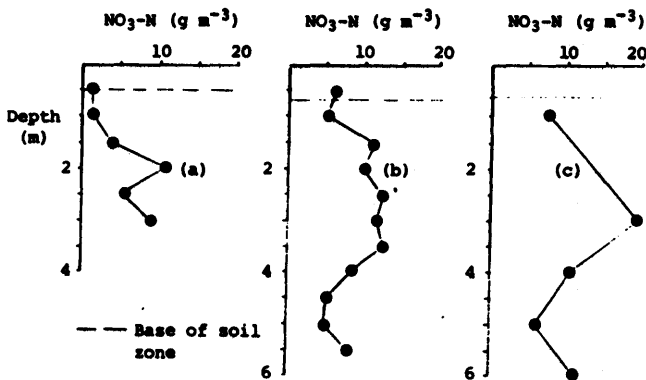


Fig. 2: Distribution of nitrate-N concentrations in unsaturated gravels beneath: (a) and (b) non-irrigated pasture on the Heretaunga plains and (c) irrigated pasture on the mid-Canterbury plains.

QUANTITY OF NITRATE LEACHED TO GROUND WATER

Field studies to measure the quantity of nitrate leached from pastureland have been conducted on the Heretaunga (Burden, 1980) and mid-Canterbury plains (Quin and Burden, 1979). Nitrate-N concentrations were measured in porewater taken from vertical profiles through unsaturated alluvium above the aquifers. Some examples are given in figure 2. Although nitrate concentrations in drainage from non-irrigated and irrigated pasture are similar, a larger volume of drainage and, therefore a greater quantity of nitrate is leached from the irrigated pastures. From mean profile concentrations and estimates of mean annual drainage, nitrogen leaching losses of $15\text{--}20 \text{ kg ha}^{-1} \text{ a}^{-1}$ from non-irrigated pasture and about $65 \text{ kg ha}^{-1} \text{ a}^{-1}$ from irrigated pasture were computed for the Heretaunga Plains. Similar calculations for the mid-Canterbury Plains indicated leaching of about $70 \text{ kg ha}^{-1} \text{ a}^{-1}$ from irrigated pastures.

If drainage directly displaced (piston-like) water previously held in the unsaturated alluvium, then a drainage front for a particular year would have moved 2.0–2.5 m below the base of the soil zone by the end of winter (when the profiles were sampled). The concentration profiles document (Fig. 2), therefore, the progressive depletion and redistribution of soil-zone nitrate through winter. Although a seasonal pattern of nitrate concentrations is retained in the unsaturated alluvium, when drainage reaches ground water, the concentration pattern would be out of phase with the season being experienced at the land surface because depth to water table is spatially variable. The seasonal trend in groundwater nitrate concentrations (Fig. 1) must, therefore, result almost exclusively from temporal variation in the volume of drainage entering ground water.

The quantity of nitrate leached from pastureland may also be estimated by balancing the major nitrogen inputs to and outputs from a pasture root zone.

Examples of generalised nitrogen balances for non-irrigated and surface-irrigated pasture are given in figure 3.

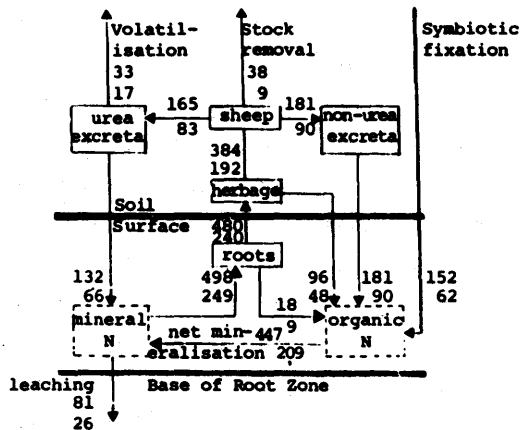


Fig. 3: Estimates of major nitrogen fluxes (kg ha⁻¹) for surface-irrigated pasture assuming herbage N is 4% by weight non-irrigated and dry matter production is 12000 kg ha⁻¹ a⁻¹ for surface-irrigated and 6000 kg ha⁻¹ a⁻¹ for non-irrigated pasture respectively.

Fixation of atmospheric nitrogen by clover is the only significant input to the system. Major outputs include removal by stock, leaching and volatilisation. Nitrogen loss by denitrification is likely to be small in the shallow, well-drained soils of the lowland plains although no conclusive field evidence is available. Leaching is the principal pathway for nitrogen loss and, as might be expected, becomes more dominant under irrigation. Approximately 23 percent (81 kg ha⁻¹ a⁻¹) of the nitrogen excreted by sheep grazing surface-irrigated pasture (346 kg ha⁻¹ a⁻¹) is leached to ground water. The leaching loss from non-irrigated pasture is about 15 percent of the excreted nitrogen. The estimates of leaching derived from the nitrogen balance computations are in close agreement with the field measurements. Clearly, nitrogen recycling by grazing stock is quite inefficient.

CONCLUSIONS

Urine voided by grazing stock is the principal source of nitrate in alluvial aquifers located beneath lowland plains in New Zealand. Surface irrigation increases 3 to 4 fold the quantity of nitrate leached from pasture by permitting higher stocking rates and by enhancing water movement through the soil zone.

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THE DISTRIBUTION OF AGRICULTURAL SOIL LEACHATES IN THE UNSATURATED ZONE OF THE BRITISH CHALK

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ABSTRACT

In Europe the Chalk constitutes a major source of potable water supply. Its outcrop forms extensive tracts of agricultural land, where the groundwater resources largely originate as infiltrating excess rainfall. Research on the unsaturated zone of the aquifer beneath such cultivated land should allow an assessment of nutrient leaching losses from the associated highly-permeable soils and the prediction of future groundwater quality trends. Pore-water profiles for nitrate, and numerous other constituents, from a site of exceptionally detailed study are presented, and compared to results from sites elsewhere in eastern England, to demonstrate the impact of modern arable agriculture. Environmental isotopes have also been investigated in depth to aid the study. The problems in evaluating the evolution of the unsaturated zone profiles are discussed.

INTRODUCTION

General Background

In the last few years, a number of papers have been published reviewing the progress of British research into the impact of agricultural practices on groundwater quality (Foster & Young, 1979 & 1980; Oakes et al, 1981; Foster et al, 1982). Their conclusions can be thus summarized:

- (a) Modern arable farming practice is leading indirectly to major leaching of nitrate, and other solutes, from the freely-drained soils characteristic of the main aquifer outcrops.

- (b) The chemical quality of groundwater supplies pumped from the main aquifers has, in most cases, only recently begun to reflect the radical changes in arable agriculture that were initiated some 20-30 years ago; this is the combined result of delayed soil response, a significant or dominant component of slow solute migration in the unsaturated zone and considerable dispersion during lateral flow to production boreholes in the saturated zone.
- (c) The detailed model of solute transport in both the unsaturated and saturated zones of the main (porous, fissured, bedrock) aquifers and the significance of in-situ denitrification require clarification by further investigation and long-term monitoring of solute and isotope distributions.

Of greatest, and most immediate, concern are numerous regions of eastern England, where most land is now used for near-continuous cereal cropping sustained by large applications of inorganic fertilizers. A single annual crop, generally sown in October or March, is cultivated without significant irrigation. Rainfall averages 600-800 mm/a, potential evapotranspiration 450-550 mm/a and excess rainfall 150-300 mm/a, the latter generally occurring in the months November-March.

Research Site Conditions

This paper discusses primarily the results of unsaturated zone investigations at a site on the Chalk near Cambridge (known locally as Fleam Dyke). The site is 60 m sq and part of a large flat field, fairly typical of agricultural land on the aquifer outcrop in eastern England, which has been in arable farming for at least 40 years. Fifteen cereal crops were cultivated during the period 1960-80 with inorganic fertilizer applications mainly in the range 60-100 kg N/ha/a, and 40-55 kg/ha/a of both P_2O_5 and K_2O , higher rates being applied in split application to winter-sown cereals. Sugar beet and peas have been the only other crops. Fertilizer application rates are

believed to have increased greatly during the period 1950-60 with increasingly frequent cereal cropping and, at this site, have been reduced marginally since 1975. Cambridge is one of the driest parts of eastern England and the site is estimated to have a long-term average excess rainfall of about 170 mm/a. In recent years climatic conditions have been extreme, the prolonged drought which ended in autumn 1976 being followed by three unusually wet winters and springs, with, for example, major infiltration occurring as late as May in 1978.

Hydrogeologically the site is on Middle Chalk with a groundwater table not thought ever to rise above 15 m depth. The Chalk is a pure, highly porous, limestone, but at this site, as in much of eastern England, it is slightly more marly and less homogeneous (Fig. 1) than the Upper Chalk of southern England. Beneath the thin (0.3 m) cover of loamy calcareous soil, the Chalk is deeply-cryoturbated to a depth of about 2.0 m (Fig. 1); the basal part of this structureless zone being exceptionally marly and underlain by a 0.5 m thick harder bed of lower porosity. The exceedingly small pore sizes of the Chalk matrix (Fig. 1) mean that hydraulic conductivities are very low (less than 10^{-3} m/d at saturation) and that gravity drainage is almost entirely inhibited, the Chalk matrix remaining very close to saturation below 1.5 m depth, the zone of plant influence. In excavations the Chalk can be seen to be traversed by a large number of high-angle joints, whose net affect is to produce a broken aspect with individual blocks commonly less than 50 mm size. The resulting system of fine fissures is believed to be characterized by apertures of 0.05-5.0 mm.

Investigation Methods

It has not proved feasible to operate suction samplers in the Chalk unsaturated zone and all samples have been obtained by destructive methods. In the case of the Cambridge site, dry percussion sampling with a drive core barrel was employed, but elsewhere air-flush rotary drilling with a lined double core barrel was necessary. All samples were very carefully handled and stored to minimize evaporation and contamination prior to analysis. Pore water from selected

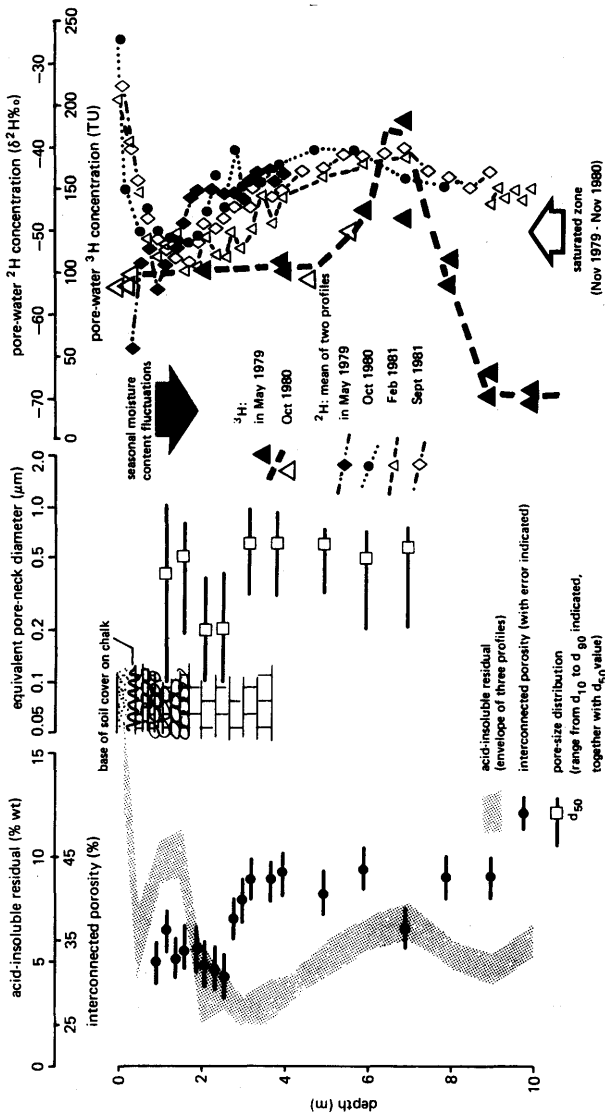


Figure 1: Geohydrological and isotopic profiles of the Chalk unsaturated zone at Cambridge site

depth intervals was extracted by high-speed centrifugation (except in the case of tritium samples where vacuum distillation to complete dryness was preferred) and analyzed by a range of automated standard chemical and isotopic techniques adapted for small volume water samples.

Water & Solute Movement

Soil physics research has also been carried out at the site; in-situ measurements of unsaturated hydraulic conductivity, soil moisture content and potential allowing computation of unsaturated zone water fluxes and pathways (Wellings et al, 1982.) In summary, the Chalk unsaturated zone pore water, to which the solute profiles relate, is believed to be relatively immobile below about 1.5 m depth, with downward solute transport controlled by a mechanism involving exchange, through lateral molecular diffusion, between the pore water and mobile microfissure water (Foster, 1975). Thus, intermittently, solutes are eluded from high concentration "regions" in the matrix and transferred to lower concentration "regions" along the flow direction. This mechanism is sensitive to variations in rate and duration of fissure flow (a function of intensity of infiltrating rainfall), fissure geometry, matrix porosity and aqueous diffusion coefficient (Barker & Foster, 1981). Non-dispersive solute movement in such a formation is a rather special case. Conversely, a complete "by-pass" of this slow mode of solute movement can occur when the infiltration capacity of the microfissure system is exceeded, the resulting further decrease in soil moisture potential allowing very rapid, short duration, groundwater flows in the macrofissures. It should be noted that a different mechanism of water and solute transport may be operative in other areas, especially on the Chalk of southern England (Wellings et al, 1982).

Nitrogen Species

Six $\text{NO}_3\text{-N}$ profiles were determined during initial investigation in May 1979. The shape of each profile was remarkably similar but laterally, at the same depth, concentrations varied quite widely (Fig. 2). The profiles revealed very high $\text{NO}_3\text{-N}$ concentrations with a "front" of major proportions at 4–8 m depth. Over the depth range to the base of the front (at 8 m) the profiles contain more than 1100 kg $\text{NO}_3\text{-N/ha}$. Comparable profiles but with generally lower concentrations and deeper fronts (Table 1) have been observed in numerous arable fields in two other regions of eastern England (Foster et al, 1982). Evidence for the movement of the profiles during the period May 1979–September 1981 is not conclusive, although little was expected

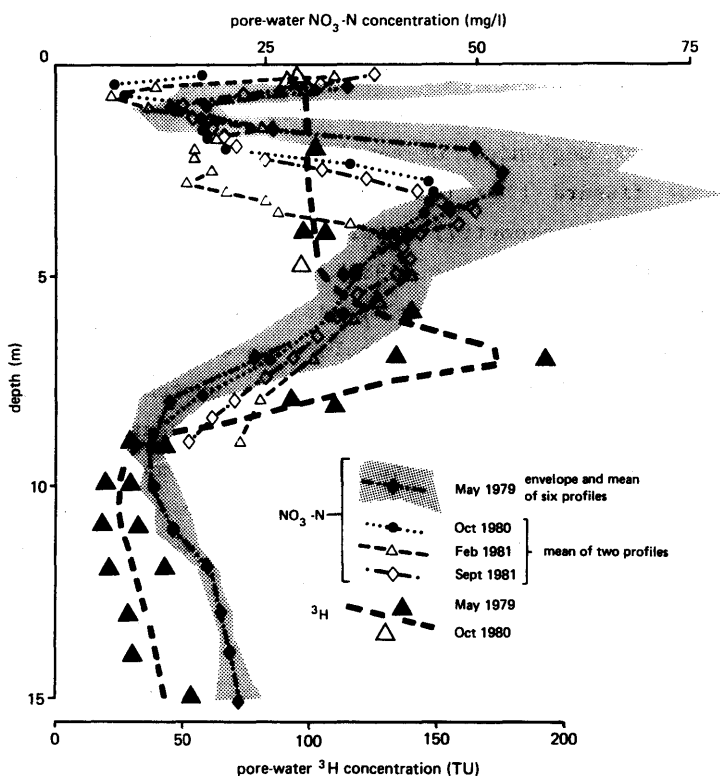


Figure 2: $\text{NO}_3\text{-N}$ profiles of Chalk unsaturated zone at Cambridge site

Table 1: Summary of chemical pore-water profiles in Chalk unsaturated zone beneath long-standing arable land

LOCATION (date)	CONCENTRATION (mg/l)	NO ₃ -N	SO ₄	Cl	Ca
Cambridge† (1979-81)	peak uniform (at depth)	40-70 15 (8 m)	170-210 50 (12 m)	80-140 40 (6 m)	210-250 ? (9+m)
North-West Norfolk (1976-79)	peak uniform (at depth)	20-40 15 (15 m)	90-160 30 (18 m)	<100* 40 (15 m*)	110-160 80 (15 m)
East Yorkshire (1978-79)	peak uniform (at depth)	<50* 15 (12 m*)	<130* 50 (18 m*)	<80* 30 (15 m*)	<160* 90 (15 m*)

† see Fig. 2 & 4 for actual profiles of NO₃-N, SO₄, Cl

* highest concentrations in upper part of profile but peak not clearly defined

since the infiltration could not have exceeded 260 mm, equivalent to the moisture content of less than 1 m depth of Chalk. The dominant feature is temporal variation of concentration not only in the sub-soil but throughout the uppermost 4-5 m of the profile (Fig. 2). This might be attributed to natural lateral site variations and/or to in-situ denitrification. Although the latter appears unlikely it cannot be discounted, since significant (insoluble) organic carbon and some nitrate-reducing bacteria have been identified at depth in

the Chalk unsaturated zone at some other sites (Whitelaw & Rees, 1980). Pore-water $\text{NH}_3\text{-N}$ concentrations in excess of 0.1 mg/l have been recorded at the research site in the depth range 0-1.0 m and 3.0-4.5 m and must reflect much higher concentrations in the absorbed phase. Although the overall form of the $\text{NO}_3\text{-N}$ profiles is broadly consistent with increasing leaching losses resulting from increased post-1960 use of inorganic fertilizers, the depth and magnitude of the peak concentrations are difficult to account for by any relatively simple model of soil nitrate availability and unsaturated zone solute movement.

Environmental Isotopes

The ^3H profiles (Fig. 2) show the characteristic "peak" which must have originated from fallout in the spring rain of 1962, 1963 and 1964. However, the "Peak" at this site is at shallower depth (5-8 m) and less defined than at some other sites.

The interpretation of such profiles from three sites on the British Chalk has been comprehensively discussed by Foster & Smith-Carington (1980) and their observations are relevant at this site also. If a non-dispersive ("piston-wise") downward movement of ^3H is assumed, post-1961 ^3H would be considered to occupy the uppermost 8 m of the Cambridge profiles and would total some 330 TUm, in about 2700 mm of water. Accepting the uncertainty about ^3H fallout in the rainfall at this site, it is still only possible to approach a satisfactory mass balance (between the profile ^3H and infiltration) if a considerable proportion of summer rainfall penetrates to 2 m depth or more and resides for sufficient time, in contact with the moisture "buffer" retained at higher tensions, for isotopic and solute compositions to equilibrate (i.e. a "soil moisture store" considerably greater than 500 mm is operative). Even given the operation of this mechanism the ^3H concentrations in the upper most 3 m of the profiles are high when compared to those of post-1975 rainfall in eastern England, which only occasionally exceed 100 TU. The reason for this important anomaly is still under investigation.

The overall shape of the profiles from this site, and the difficulty in simulating their major features with any simple model of the input

and transport mechanisms, suggest that the downward movement of ^3H below a depth of 2-3 m is also somewhat dispersive, with characteristic "forward tailing" and "peak retardation" (Barker & Foster, 1981). The stable isotope ratios ($^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$) have also been investigated. Large seasonal fluctuations in the isotopic composition of rainfall have been measured at the site, with isotopically-light rainfall in the winter months, but a fairly constant long-term weighted annual mean is assumed.

The most significant features of the results are:

- (a) Apparent discrepancy between the weighted mean composition of recent rainfall ($\delta^2\text{H} = -60$ ‰; $\delta^{18}\text{O} = -8.5$ ‰) and the uniform composition of unsaturated zone porewater (below about 3 m depth), the drainage of a 5 m deep lysimeter on an adjacent grass site and the local saturated zone groundwater (Fig. 3).
- (b) Variable composition of the uppermost 2-3 m of the profile; the shift in composition from isotopically light in May 1979 to heavy in October 1980, for example, being marked (Fig. 1).

The results suggest a mechanism which produces a "selective" net infiltration of isotopically-heavy water relative to average rainfall

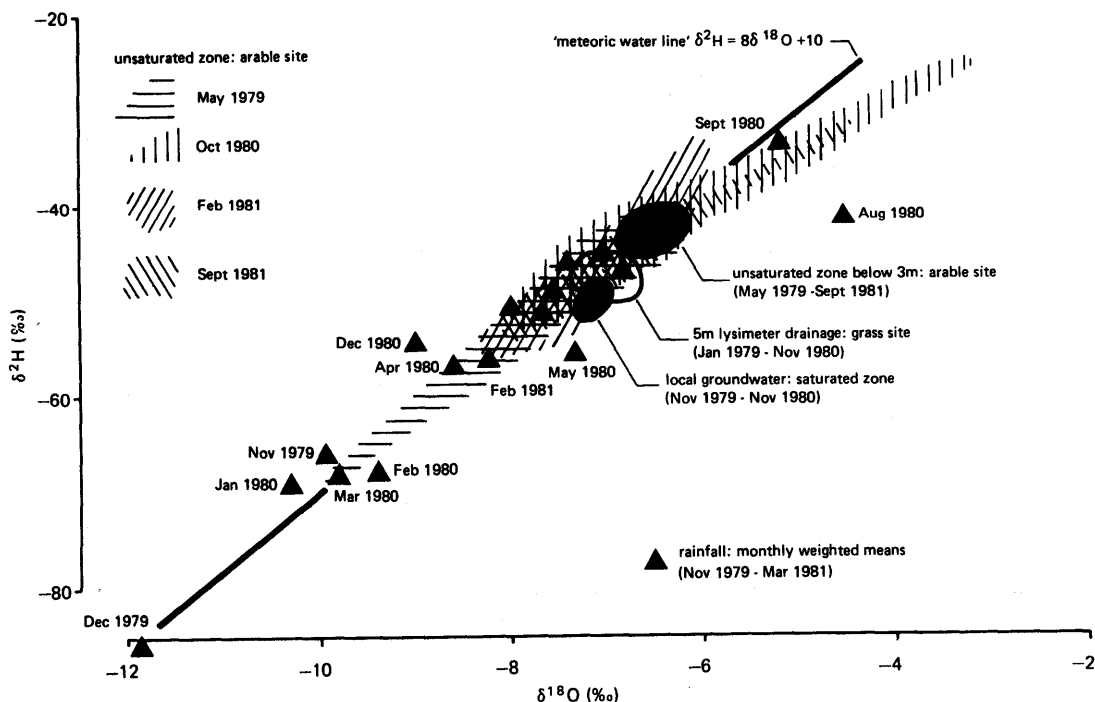


Figure 3: Summary of stable isotope data for Cambridge Chalk site

and support the concept of rapid penetration of summer rainfall, and mixing with "stored" soil moisture prior to evapotranspiration, over the uppermost 2 m or so of the profile. At other sites with more clearly defined ^3H peaks small cyclic variations in $\delta^{2}\text{H}$ and $\delta^{18}\text{O}$, of seasonal origin, occur over some meters depth (Bath et al, 1982), suggesting less mixing in the upper zone.

Chloride

The pore water profiles for a non-reactive, conservative ion, such as Cl also aid the interpretation of solute movement. Botanically, chloride is a non-nutrient, although it may be taken into some root crops (notably sugar beet) and plant saps.

The Cl profiles for the Cambridge site exhibit a similar form to those for $\text{NO}_3\text{-N}$, but with a somewhat narrower peak (Fig. 4). The Cl fallout in rain leads, after soil concentration, to a groundwater composition of some 15 mg/l and all Cl above this background must be

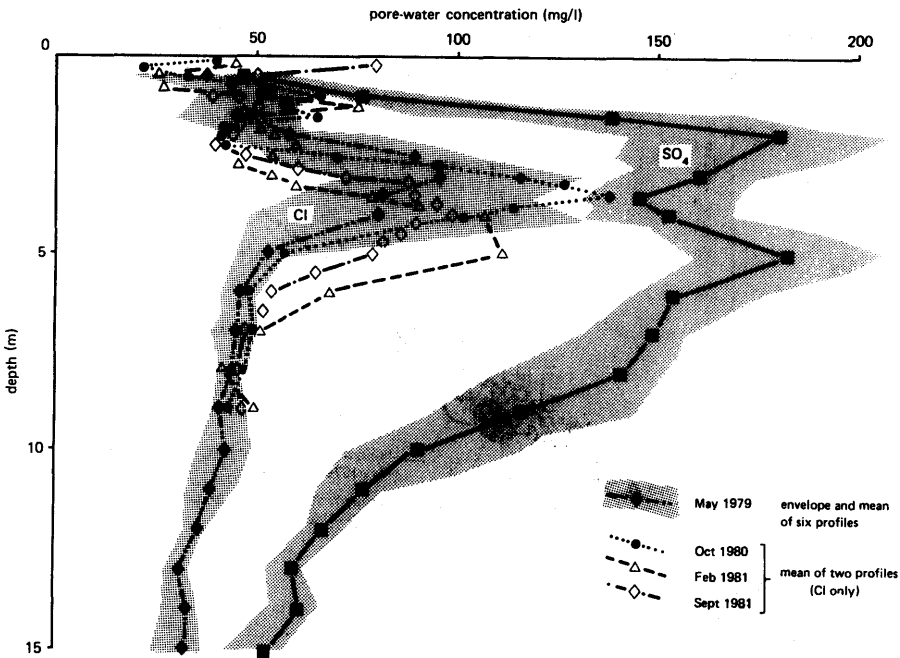


Figure 4: Cl and SO_4 profiles on Chalk unsaturated zone at Cambridge site

derived from potash fertilizer (almost invariably KCl) and certain other soil treatments.

In common with the $\text{NO}_3\text{-N}$ and ^3H profiles, when a non-dispersive downward movement is assumed, some problems of interpretation arise and also argue against this simple model of solute migration:

- (a) The mass of Cl above "rainfall background" to 8 m depth in the profile, (over 1300 kg/ha) is considerably more than the total applied since 1961 in fertilizers, some 900 kg/ha.
- (b) The profile shape is not consistent with the historic record of fertilizer applications, particularly in respect of the peak width and magnitude.

Ca-CO₃-SO₄ Equilibria

Very high concentrations of SO_4 in porewater profiles, with a major "front" in the depth range 5-12 m, have been detected (Fig. 4); the Ca profiles are similar to those for SO_4 . Comparable profiles have been observed at numerous arable sites in other regions (Table 1). Although the fallout of SO_4 in rain has increased significantly in recent years, it is still only sufficient at the Cambridge site to generate groundwater concentrations of 30-40 mg/l.

The unstable parameters pH and HCO_3 were not measured in the Cambridge profiles, but on-site determinations for five boreholes in other regions (whose reliability was confirmed by excellent overall analytical balances) show the unsaturated zone pore waters to be mostly supersaturated with respect to CaCO_3 (indices of +0.1 to +0.6) and grossly undersaturated with respect to CaSO_4 (indices of -0.8 to -1.9). In these profiles the CaSO_4 stoichiometry can be evaluated by subtracting Ca due to CaCO_3 dissolution. The approximate correlation between (Ca-HCO_3) and SO_4 , their proportions not exceeding Ca-SO₄ equivalence, suggests that CaSO_4 is an important source of SO_4 . Marine carbonate rock, such as the Chalk, may contain up to 0.05% S by weight, but this is unlikely to have been the source of these porewater SO_4 concentrations. The CaSO_4 is probably derived from fertilizers and its rapid dissolution with CaCO_3 may account for CaCO_3 supersaturation: SO_4 is present in large quantities in some types of inorganic fertilizers, notably $(\text{NH}_4)_2\text{SO}_4$ and

$\text{Ca}(\text{H}_2\text{PO}_4)_2\text{-CaSO}_4$, although the usage of both types has decreased in recent years. The rate of migration of SO_4 will be influenced by its lower diffusion coefficient and by anionic retention.

Table 2: Summary of minor and trace element porewater profiles from Chalk unsaturated zone beneath Cambridge arable site

ELEMENT	DETECTION LIMIT (mg/l)	UNIFORM CONC.* (mg/l)	PROFILE FORM		PEAK CONC. (mg/l)
			SOIL TAIL	PEAK (m)	
Na	0.5	20.0	yes	no	-
Mg	0.1	2.5	no	2-5	4.0
Si	0.1	2.5	yes	no	-
B	0.02	0.35	yes	no	-
K	0.5	0.5 - 2.0	no	no	-
Ba	0.001	0.2	yes	no	-
Sr	0.001	0.5 - 0.6	no	?	1.0
Cu	0.005	0.01- 0.03	no	2-5	0.06
Zn	0.01	0.02	no	2-5	0.05
Li	0.005	0.01	no	no	-

* approximate value for two detailed profiles to 9 m in 1981 given, or range where results have considerable scatter without trend
n b: in all samples analyzed following elements were below detection limit indicated in parenthesis in mg/l: Pb (0.2), Al (0.1), Mo (0.1), Ni (0.05), Co (0.02), Cd (0.005), Fe (0.005), Mn (0.005), V (0.005).

Minor & Trace Elements

Amongst the profiles for these elements four groups can be distinguished (Table 2):

- (a) Profiles with indications of peak concentrations at depths of 2-5 m similar to Ca and/or SO_4 and/or Cl and/or $\text{NO}_3\text{-N}$.

- (b) Profiles which "tail" to uniform concentrations from maxima at the base of the soil.
- (c) Elements which exhibit relatively uniform concentrations throughout the profiles.
- (d) Elements which do not exceed current detection limits.

Some correlation of Mg, Sr, Zn (and perhaps Cu) with Ca is not surprising since they are characteristically associated with the carbonate phase. Correlation in turn with Cl and $\text{NO}_3\text{-N}$, which are largely fertilizer derived, may result from the latter modifying the hydrochemistry (especially pH) of water infiltrating the Chalk surface and allowing greater reaction with carbonate minerals, releasing more Ca, Sr, Mg, Zn and Cu before equilibrium is achieved, or from their presence in fertilizers.

The relatively high concentrations of Ba and B in the uppermost part of the profiles (Table 2) are probably fertilizer derived, but their migration must have been strongly retarded by adsorption-desorption processes on soil minerals

CONCLUSION

Large quantities of solutes leached from arable land are present in the unsaturated zone of the British Chalk. The rates of leaching have increased substantially with more intensive cultivation over the last 20 years or so. The pore water profiles presented also demonstrate the complexity of solute transport mechanisms (from the soil through the unsaturated zone) in a fissured microporous limestone, such as the Chalk. These mechanisms need to be better understood if the historic and future evolution of the major fronts of nitrate, sulphate and other solutes are, respectively, to be evaluated and predicted. From the numerous lines of investigation pursued in detail at the Cambridge site it is suggested that:

- (a) In the uppermost few meters, the precise depth being a function of the hydrogeological properties of the weathered profiles, solute movement is strongly dispersive, with intermittent rapid downward (and, presumably, near-continuous slow upward) fluxes occurring in summer.

- (b) Solutes are eluded from this upper zone and transported downwards by infiltrating excess rainfall, the extent of non-equilibration, or dispersion being essentially a function of the intensity of infiltration, the matrix hydraulic properties, the fissure geometry and the appropriate diffusion coefficient of the solute concerned.

Environmental isotopes have proved a considerable aid in evaluating both the input and transport processes, which can be expected to vary significantly across and between regions.

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PREDICTION OF VARIATIONS IN GROUND-WATER QUALITY UNDER THE INFLUENCE OF PEN SEWAGE IRRIGATION

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ABSTRACT

This paper deals with the problems of variations in ground-water quality under the influence of pen sewage irrigation (arrival time of the sewage reaching the ground-water level, time variations of the concentration of pollutants in ground-water) and of the conditions for ground-water pollution control.

GENERAL STATEMENTS

The influence of large pens on the environment is equal to that of industrial enterprises. Large amounts of waste (manure) are accumulated in these pens, and disposal is a very complicated problem. One of the means of disposal of the pen waste is by the use of diluted pen waste for the irrigation of the fields of the same pen where the forage crops are cultivated. In this case, environmental and, primarily, ground-water pollution can take place. Ground-water pollution, in its turn, can lead to the loss of water supplies and the pollution of rivers and water reservoirs by draining ground-water.

Thus, the possibility of pen sewage irrigation is considerably determined by its ability to pollute groundwater. Very often this factor is the determinant one, when designing the pens.

Nitrogen, phosphorus and potassium are the main pollutants of pen waste affecting ground-water; the same substances are nutrients for

the vegetation. With soil fertilization phosphorus is fixed very quickly, so its losses in the leaching process are negligible. Phosphorus movement downward through the soil horizon is an insignificant one; it does not reach the ground-water level. Potassium replaces cations of Ca and Mg, when dressing and, thus, it is not harmful for ground-water. Nitrogen compounds, particularly nitrates, are the main pen pollutants affecting ground-water.

Nitrogen is contained in liquid manure in the form of various compounds, including the ammonium form (NH_4). Ammonium nitrogen is converted into nitrites, and nitrites into nitrates by the process of nitrification. Migration of nitrogen compounds from the Earth's surface to the groundwater level is a very complicated process as a result of the processes of nitrification and denitrification.

In the upper soil horizons and at ground surface ammonium nitrogen is successively converted into nitrites and nitrates, as noted by S.Gazda and Yu.Stibral.

When migrating further downward through the soil profile, nitrates can be affected by the process of denitrification, due to which their amount will decrease.

Besides nitrogen, phosphorus, potassium and some other chemical components, pen waste contains considerable quantities of various microorganisms (bacteria of the coliform bacillus group, pathogenic enterobacteria, etc.). Thus, ground-water located in the areas with pen sewage irrigation can be polluted by bacteria as well as with nitrates.

Due to a considerably low survival rate of microorganisms in ground-water, their migration through the ground-water aquifer is insignificant. Usually bacterial pollution is localized in the area, immediately confined to the pollution source.

According to the data of A.K. Oradovskaya and E.I. Molozhavaya (1977), the time of the survival rate of particular microorganisms in

ground-water is characterized by the following figures:

coliform bacillus and enterobacter (bacteria count $10^5 - 10^6$ per liter)	- 400 days
typhoid salmonella (10^2 b/l)	- 50 days
(10^4 b/l)	- 120 days
V-paratyphoid salmonella (10^2 b/l)	- 220 days
(10^4 b/l)	- 70-400 days

All the figures from the above table should be considered as relative ones. They can vary, depending on the character of environment and the state of microorganisms. For example, under the conditions of low temperature ($4-8^{\circ}\text{C}$) microorganisms preserve their viability for a long period of time.

It should be noted that ground-water containing certain detergents (for example, sulphand NP-1) and phenols was characterized by an increased survival rate of bacteria.

Experimental studies showed that the limited distribution distance for microorganisms is determined by their decomposition as well as by the processes of rock absorption.

The following calculated survival rates of microorganisms in ground-water can be used for the predictions of the migration of microorganisms in ground-water, according to F.M. Bochever and A.E. Oradovskaya (1972):

200 days - when penetrating from relatively slightly polluted and periodically functioning sources;

400 days - with the penetration being from highly polluted and constantly functioning sources (pens and fields irrigated by the sewage, etc.).

Thus, pen sewage irrigation can result in ground-water pollution of two types - nitrate and bacterial.

It has already been noted that the nitrate content of ground-water is affected by various factors, represents a very complicated phenomenon, and has not been studied well enough. At the same time, nitrates are the final and, totally, stable form of the nitrogen compounds. Therefore, ground-water quality prediction will include

the following, in the case of nitrate pollution:

- a) time for sewage to reach the ground-water level in the process of percolation from the Earth's surface;
- b) variations in the nitrate content of groundwater as the result of irrigation;
- c) the size of polluted areas in the ground-water aquifer.

In the case of bacterial pollution, this prediction incorporates the velocity of the sewage reaching the ground-water level and the lateral extent of the pollution in the ground-water aquifer taking into account the maximum time of bacterial survival in ground-water (400 days).

Time for the sewage to reach the ground-water level.

Sewage irrigation occurs at the area F ; discharge of the sewage in the process of irrigation Q ; thickness of the aeration zone (i.e. depth to the ground-water surface) m ; filtration coefficient and porosity of the rocks of the aeration zone K and n . If $K \geq q$, where $q = Q/F$ free sewage filtration, without water-table mounding at the Earth's surface, takes place. In this case, the time it takes for sewage to reach the ground-water level is determined according to the following formula

$$T = n.m/3 \sqrt{(q^2.K)} \quad (1)$$

If $K < q$, i.e. permeability of the underlying layer is less than the value necessary for irrigation, sewage filtration takes place, followed by the formation of a rising water table mound. In this case, the value of T is determined by the equation

$$T = m / \{ (1-n).K/2n + \sqrt{((1-n)^2 . K^2/4n^2 + q.K/n)} \} \quad (2)$$

The above formulas (1) and (2) are valid for conditions in which the aeration zone has homogeneous filtration properties. An approximate assessment of T can be performed in the above manner, if the section is heterogeneous, e.g. a double-layer one. If both of the layers satisfy the condition $K \geq q$, the time T_1 and T_2 for the sewage to

flow through each of the layers individually is performed with the formula (1). In this case, the corresponding parameters of each layer (m , K , n) are substituted into the formula, the total time T being equal to the sum of T_1 and T_2 .

When one of the layers, for example the upper one, satisfies the condition $K \geq q$, and the lower one satisfies the condition $K < q$, the time T_1 of the sewage flowing through the upper layer is determined with the formula (1); the time T_2 of the sewage flowing through the lower layer is determined using the formula (2); the total time T equals the sum of T_1 and T_2 .

In case of bacterial pollution, one can assess with a relatively high probability, whether the bacterial pollution will or will not take place in the ground-water aquifer, located under the irrigated tracts of land, comparing the time T with the time of the bacteria survival rate.

Evaluation of the variations in concentration of pollutants in ground-water.

Sewage-farms are irrigated with diluted pen sewage. The degree of dilution and the amounts of the sewage are determined by the agrotechnical conditions of the irrigated area. Usually irrigation takes place during the growing season (May - July).

A pollutant (nutrient) balance used for the sewage applied to sewage-farms, can be expressed in the following way:

$$Q = Q_p + Q_n + Q_b + Q_\varphi \quad (3)$$

where Q - total amount of pollutant (nutrient) used as fertilizer;

Q_p - amount of pollutant assimilated by plants;

Q_n - amount of pollutant remaining in soils and in the zone of aeration;

Q_b - amount of pollutant lost to the air;

Q_φ - amount of pollutant leaching through the aeration zone to the ground-water level.

It is the amount Q_{φ} , primarily, that accounts for the ground-water pollution. Additional pollution of ground-water can be caused by the leaching of residual pollutants from the zone of aeration and soils. Thus, it is necessary to know the value of Q_{φ} for the prediction of ground-water pollution under the sewage-farms. However, in many cases the other values, except for Q_p , are unknown. In this situation, one can assume the ground-water pollution to be caused by the total amount of the pollutants minus the amount of fertilizer uptake by plants, which is equal to:

$$Q_{\varphi} = Q - Q_p \quad (4)$$

Therefore, in order to study pen sewage pollution of ground-water, it is necessary to know the value of Q_p , which characterizes the amount of pollutants (nutrients) assimilated by the plants. According to data found in various texts, this value is equal to 40-60% of the initial amount of pollutant content of the sewage used for irrigation.

Concentration of the pollutants in ground-water under the sewage-farm can be evaluated on the basis of the following schematization of the seepage conditions and mixing of the sewage and ground-water.

Let a sewage-farm be in the form of a rectangle with the sides L and S ; the side L coincides with the direction of the natural ground-water flow. Seepage rate of the natural ground-water flow is $Ve = K \cdot i_e$, where K is seepage coefficient, i_e is gradient of natural flow. An average thickness of the ground-water aquifer is h , porosity of waterbearing rocks is n_o , background (natural) content of pollutants (nitrates) of ground-water is C_o .

Annually the tracts of land are irrigated with the sewage for some period of time (irrigation period). The rest of the time (to the beginning of the next irrigation) represents an interirrigation period (t_m). An average amount of the sewage (volume) applied for the fertilization of a sewage-farm during the period of irrigation is equal to W_n . It is supposed, that all of this amount of sewage is infiltrating to the ground-water level. An average concentration of the pollutants (nitrates) of the infiltrating sewage is C_{φ} .

The value of C_φ is calculated, knowing the content of nitrogen of the sewage (Q) and assimilation of nitrogen by the plants (Q_p). The difference between Q and Q_p related to W_n will be equal to the value of Q_φ .

During the period of irrigation the sewage applied for fertilization infiltrates and mixes with ground-water under the sewage-farm. During the interirrigation period the polluted water moves downward under the influence of the natural movement of ground-water. In the next irrigation period, infiltrating sewage mixes with the same volume of ground-water under the sewage-farm, which at that time consists of two parts: a mixture of unpolluted ground-water and the sewage, formed during the first period of irrigation, and unpolluted ground-water, which replaced polluted ground-water over the interirrigation period. An estimated relationship for predicting time variations in the concentration of pollutants under the sewage-farm has been made, while going on the assumption of this process for the next irrigation and interirrigation periods:

$$C_i = (W_\varphi \cdot C_\varphi + W'_0 \cdot C_{(i-1)} + W''_0 \cdot C_0) / (W_0 + W_\varphi) \quad (5)$$

where C_i - concentration of the pollutants in ground-water under the sewage-farm for any i -year from the beginning of irrigation

C_{i-1} - concentration of the pollutants in ground-water in the previous year

W_0 - volume of ground-water under the sewage-farm,
 $W_0 = L \cdot S \cdot h \cdot n_0$

W''_0 - volume of the unpolluted ground-water, which partly replaces the volume of polluted groundwater over an interirrigation period $W''_0 = S \cdot h \cdot n_0 \cdot x_m$, $x_m = Ve/n_0$

W'_0 - volume of the polluted ground-water remaining under the sewage-farm, after its replacement by the unpolluted water in the interirrigation period

$$W'_0 = S \cdot h \cdot n_0 (L - x_m)$$

The peculiarity of calculations with formula (5) consists in the following: to evaluate the concentration of pollutants in ground-water for a particular year, e.g. for the tenth year from the beginning of irrigation, it is necessary to know the pollution concentration of the previous, i.e. of the ninth year. Therefore, to predict the pollution concentration for an i -year from the beginning of irrigation, one should perform preliminary calculations ($i-1$), beginning from the first irrigation year. The concentration of pollutants after the irrigation period in the first irrigation year is equal to:

$$C_1 = (W_o \cdot C_o + W_{\varphi} \cdot C_{\varphi}) / (W_o + W_{\varphi}) \quad (6)$$

Having determined the pollution concentration of the first year of irrigation with the formula (6), one can successively evaluate concentrations for the second, the third, the fourth and for all the following years up until the required year. These calculations are very simple and easily done, though they seem to be rather complicated.

Estimated relationships for a double irrigation in the growing-season have been obtained in a similar way. The analysis of these relationships showed, that if the volume of the inflowing sewage is the same with single and double irrigation, then the difference in variations of the concentration of the pollutants in ground-water in each of the cases are negligible. Thus, it can be assumed for approximate predictions, that the sewage irrigation occurs once every period with a time amounting to the summed time of all the irrigation periods, and with the volume of irrigation sewage, equaling to the summed volume of irrigation in particular periods.

Methods for the calculation of the extent of pollutants spread over the ground-water aquifer are described in detail in the published works by F.M. Bochever and A.E. Oradovskaya (1972), V.M. Goldberg (1976) and others and, so, they are not treated here. It only should be noted, that with the absence of ground-water withdrawals, transportation of the pollutants over the ground-water aquifer, generally,

is accounted for by natural ground-water flow. With water withdrawal located near the sewage-farm, the plume of polluted water will be formed in the direction of this water withdrawal. The rate of flow of the polluted water will result in a considerable increase due to the ground-water withdrawal.

The distance of spread of bacterial pollution is estimated according to the maximum time of the bacteria survival rate in ground-water, assumed to be equal to 400 days.

When calculating the spread of pollutants through the ground-water aquifer, one should evaluate, first of all, the time it takes for the pollution front to reach the nearest ground-water withdrawals, as well as the rivers draining ground-water.

ASSESSMENT OF THE CONDITIONS FOR GROUND-WATER POLLUTION CONTROL

An assessment of the degree of ground-water protection from pollution by sewage irrigation can be estimated from the time it takes for the polluted water to reach the ground-water level in the process of seeping from the Earth's surface. This assessment is of a comparative nature. The longer the time it takes for seepage the better are the conditions for ground-water protection. An assessment of the conditions for ground-water protection, using the seepage time, is especially suitable in relation to the bacterial pollution, as well as relative to particular pesticides with known decay times.

The seepage time is calculated using the formulas (1) or (2), depending on the natural conditions of the observed region.

If the conditions for ground-water protection are evaluated without reference to specific sewage-farms then $q=0.03\text{m/d}$ can be taken as the initial value of q . The selection of this value can be accounted for by the following facts. According to F.M. Bochever and A.E. Oradovskaya (1972), sewage inflow amounts to the following are:

municipal sewage-farms	- from 10 to 30 m^3 per 1 hectare per day;
agricultural sewage-farms	- not more than 5-20 $\text{m}^3/\text{ha/day}$ and
seepage farms	- from 100 to 300 $\text{m}^3/\text{ha/day}$.

Considering these data and assuming $Q = 300 \text{ m}^3/\text{d}$ and $F = 1 \text{ ha} = 10^4 \text{ m}^2$, one can take $q = 0.03 \text{ m}^3/\text{d}$ for the estimated value of q in the process of assessing the conditions for ground-water protection. An

assumed estimated value of q is close to the maximum values of the sewage inflow in the areas of sewage-farm.

Judging from the time it takes for the sewage to reach the ground-water level, one can single out the following classes of ground-water protection:

- I $T \leq 10$ days
- II $10 \text{ days} < T \leq 50 \text{ days}$
- III $50 \text{ days} < T \leq 100 \text{ days}$
- IV $100 \text{ days} < T \leq 200 \text{ days}$
- V $200 \text{ days} < T \leq 300 \text{ days}$
- VI $300 \text{ days} < T \leq 400 \text{ days}$
- VII $T > 400 \text{ days}$

The higher the class, the better are the conditions for protection. Absolute evaluations of the degree of ground-water protection can be given relative to the particular types of the pollutants and the known time of their decay. In particular, it is related to bacterial pollution and to pollution by several types of pesticides. A map of ground-water protection would show the depths of the ground-water level location, thickness (summarized) of semi-permeable layers, seepage coefficients of rocks in the zone of aeration and, as the resultant output, characteristic-protection classes. The protection map is used to substantiate the location of sewage-farms, as well as the other operations with the aim of preventing and decreasing the extent of ground-water pollution.

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NUMERICAL SIMULATION OF THE EFFECT OF SOIL NITROGEN TRANSPORT AND TRANSFORMATIONS ON GROUNDWATER CONTAMINATION

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ABSTRACT

Two numerical models, one for the vadose zone and the other for the aquifer system are utilized to predict potential nitrate pollution in groundwater. Transport by dispersion and convection of mobile species of nitrogen, ammonium ion exchange, first order nitrogen transformations, and nitrogen plant uptake are included in the formulation for the vadose zone. Transport of nitrogen in the aquifer is assumed to be affected only by dispersion-convection phenomena. Justifications for one-dimensional conceptualization of flow in the vadose zone and two-dimensional representation for the aquifer, under various field conditions, are presented. To illustrate the concept, a simple hypothetical problem is solved. The approach presented here provides an efficient means of long-term simulation of large scale field problems.

INTRODUCTION AND OBJECTIVE

The concern over the behavior of nitrogen (N) in soil-water systems from economic and environmental considerations. Addition of agricultural sources of N to the soil system causes excess leaching of soluble N species below the active root zone. Transport of nitrates from the vadose zone to groundwater increases the concentration of nitrates in the subsurface aquifers (Ayers and Branson 1973) producing potential health hazards in living organisms (National

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Academy of Sciences 1978). Evaluation of the impact of N additives on groundwater systems requires a knowledge of the processes taking place in the unsaturated zone and transport phenomena occurring in the aquifer system.

In the last 10 years, extensive research has been conducted to study the behavior of N and its potential environmental impacts with great emphasis on transformations and transport of N in the vadose zone (Dutt et al. 1972, Mehran and Tanji 1974, Duffy et al. 1975, Davidson et al. 1978, Tanji and Mehran 1979). However, the interaction between the unsaturated zone and the underlying aquifer system has received less attention.

Uneven distribution of irrigation and precipitation, spatial variability of physicochemical properties of soils, and non-uniformity of vegetative cover are the primary causes of three-dimensional transport of water and solute in the vadose zone (Nielsen et al. 1980). However, under some special and practical circumstances, the three-dimensional description of transport can be reduced to a one-dimensional representation. Such is the case in relatively homogeneous fields of large areal extent with uniform vegetative cover which are the conditions generally encountered in large-scale agricultural practices. Furthermore, considering the complexity of the processes occurring in the vadose zone, the assumption of one-dimensionality of transport in the formulation results in considerable reduction in computer time and storage requirement. It is believed, that for large scale field problems of our interest the advantages of one-dimensional description of transport in the vadose zone far outweighs the gains in multidimensional description of transport processes.

Under the most general conditions, fluid flow and solute transport within an aquifer are also three-dimensional phenomena. However, presence of favorable conditions allows two-dimensional considerations. In cases of linear sources of contamination such as wells, streams, etc., the transport of the solute can be investigated in two-dimensional vertical cross sections containing the plane fluid flow field. Areal analysis of solute transport lends itself to the

assumption of either total mixing in depth at every point, in the aquifer, or practically no mixing. Injection of contaminants through fully penetrating wells or percolation of leachates from agricultural activities can create such conditions. However, the reality of most field situations lies somewhere in between the two extremes and therefore, the accuracy of two-dimensional model applications would depend on the closeness to the two limits. One-dimensional representation of flow in the vadose zone combined with two-dimensional conceptualization in the aquifer is believed to give a realistic description of transport in the overall flow region. The thrust of the proposed work is based on this concept.

The objective of this paper is to present a model for N transport and transformations to predict the migration of nitrates in both the vadose zone and the underlying aquifer system as influenced by agricultural and groundwater management parameters. The model can be used to predict long-term impacts of agricultural activities on possible groundwater contamination and evaluate the effects of present or future groundwater management alternatives.

THE MODEL

The present model describes simultaneous transport of water and soluble N species in saturated-unsaturated porous media. The flow region consists of an aerated zone referred to as vadose zone and the underlying saturated aquifer system. The processes contributing to change in concentration of nitrates in the vadose zone include: dispersion-convection, plant uptake, ion exchange and N transformations. These transformations consist of nitrification, denitrification, mineralization and immobilization. The concentration of nitrate in the aquifer is assumed to be affected only by dispersion-convection phenomena. In the following sections, the governing equations for the transport of water and soluble N species are presented in a generalized two-dimensional form for the entire flow region. However, in applying the equations to the vadose zone, we should bear in mind that the horizontal components of flow will vanish.

Water Flow

Using Darcy's law and principle of conservation of mass, the governing differential equation describing the isothermal movement of water in a saturated-unsaturated medium can be written as

$$\begin{aligned} ((\theta/n) \alpha + \beta + c) \partial h / \partial t = \partial / \partial x (K_{xx} (\partial H / \partial x) + K_{xz} (\partial H / \partial z)) \\ + \partial / \partial z (K_{zx} (\partial H / \partial x) + K_{zz} (\partial H / \partial z)) - W(z, t) \end{aligned} \quad (1)$$

where, θ = water content, n = porosity, α , β = modified coefficients of compressibility for medium and water, c = soil moisture capacity, h = pressure head, t = time, x , z = cartesian coordinates, k_{xx} , k_{zz} , K_{zx} , K_{xz} = hydraulic conductivity tensor components, H = hydraulic head, $W(z, t)$ = plant water extraction. In applying eq. (1) to the vadose zone, the compressibility terms vanish while the soil moisture capacity and plant water extraction terms assume positive values. On the other hand, when eq. (1) is applied to the saturated aquifer system, c and $W(z, t)$ both approach zero.

Initial and Boundary Conditions

Under field conditions, eq. (1) is subject to a set of general initial and boundary conditions as follows:

$$h(x, z, 0) = h_0(x, z, 0)$$

$$h(x, z, t) = h_1 \text{ on } A_1 \times t [0, \infty)$$

(Dirichlet boundary condition or first kind)

$$-(K_{xx} (\partial h / \partial x) + K_{xz} (\partial h / \partial z) + K_{zx}) \cdot n_x - (K_{zx} (\partial h / \partial x) + K_{zz} (\partial h / \partial z) + K_{zz}) \cdot n_z = q_2 \text{ on } A_2 \times t [0, \infty)$$

(Neumann boundary condition or second kind)

$$h(x, z, t) = h_3$$

or

$$-(K_{xx} (\partial h / \partial x) + K_{xz} (\partial h / \partial z) + K_{zx}) \cdot n_x - (K_{zx} (\partial h / \partial x) + K_{zz} (\partial h / \partial z) + K_{zz}) \cdot n_z = q_3 \text{ on } A_3 \times t [0, \infty) \quad (2)$$

(Cauchy boundary condition or third type)

A_1 , A_2 and A_3 denote different parts of the boundary where various boundary conditions exist. n_x and n_z are the directional cosines of the outward unit vector normal to the corresponding surface of the boundary. The known quantities on the right hand side of the equations are identified by () mark.

Nitrogen Flow

Transport of soluble N species under isothermal saturated-unsaturated flow field in two-dimensional Cartesian coordinate system can be expressed as

$$\begin{aligned} \partial / \partial t (\theta C_i + \rho_b S) = \partial / \partial x (\theta D_{xx} (\partial C_i / \partial x) + \theta D_{xz} (\partial C_i / \partial z) - q_x C_i) \\ + \partial / \partial z (\theta D_{zx} (\partial C_i / \partial x) + \theta D_{zz} (\partial C_i / \partial z) - q_z C_i) \\ - C_i W(z, t) - \sum K_{ij} C_i + \sum K_{ji} C_j \quad i \neq j \end{aligned} \quad (3)$$

where, C_i = concentration of i th species in solution phase, ρ_b = bulk density of medium, S = amount of solute in the adsorbed phase, D_{xx} , D_{xz} , D_{zx} , D_{zz} = dispersion coefficients, q_x, q_z = Darcy velocities, K_{ij}, K_{ji} = transformation rate constants.

$$S = K_d C_i \quad (4)$$

where K_d is the distribution coefficient. Substituting eq. (4) into eq. (3) results in a governing equation with only one dependent variable to be solved:

$$\begin{aligned} \Theta R_d (\partial C_i / \partial t) = & (\partial / \partial x) (\Theta D_{xx} (\partial C_i / \partial x) + \Theta D_{xz} (\partial C_i / \partial z) - q_x C_i) \\ & + \partial / \partial z (\Theta D_{zx} (\partial C_i / \partial x) + \Theta D_{zz} (\partial C_i / \partial z) - q_z C_i) \\ & - C_i W(z, t) - \sum_{i \neq j} K_{ij} C_i + \sum_j K_{ji} C_j \end{aligned} \quad (5)$$

where,

$$R_d = 1 + (\rho_b K_d / \Theta) \quad (6)$$

is the retardation factor. The ammonium ion is the only N species that is subject to adsorption.

The dispersion coefficients are expressed by (Bear 1972):

$$\Theta D_{ij} = (a_T q + D_m \tau) \delta_{ij} + (a_L - a_T) q_i q_j / q \quad (7)$$

where, i, j indicate cartesian coordinates x, z , D_m = molecular diffusion coefficient, $q = (q_x + q_z)^{1/2}$, a_L, a_T = longitudinal and transverse dispersivities, τ = tortuosity, and δ_{ij} = Kronecker's delta function.

The term $C_i W(z, t)$ in eq. (5) denotes the mass of solute extracted by plant roots. It is, therefore, assumed that the only mechanism of absorption of soluble N species is through mass flow of water across the plant roots. Comparisons between measured nitrate uptake and computed values obtained from conceptual N models substantiate the validity of the above assumption (Tanjfi et al. 1979, Mehran et al. 1981).

Nitrogen Transformations

Depending upon environmental conditions, various N transformation processes will take place in the vadose zone with different intensities. The simplified pathways of important transformations in an elemental volume of soil are shown in figure 1 where nitrification, denitrification, and immobilization processes are selected as dominant mechanisms of N transformations.

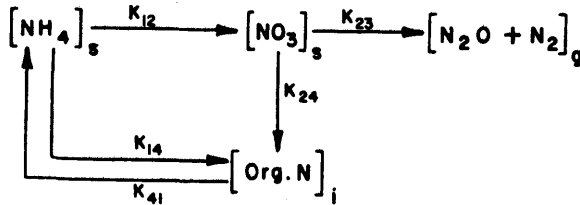


Fig. 1 Nitrogen transformations pathways

Assuming all reactions in figure 1 obey the first order kinetics, the mathematical model describing transformation processes can be expressed by a system of differential equations as follows (Mehran and Tanji, 1974):

$$d[\text{NH}_4^+]_s/dt = - (K_{12} + K_{14}) [\text{NH}_4^+]_s + K_{41} [\text{Org.N}]_i \quad (8)$$

$$d[\text{NO}_3^-]_s/dt = - (K_{23} + K_{24}) [\text{NO}_3^-]_s + K_{12} [\text{NH}_4^+]_s \quad (9)$$

$$d[\text{Org.N}]_i/dt = - K_{41} [\text{Org.N}]_i + K_{14} [\text{NH}_4^+]_s + K_{24} [\text{NO}_3^-]_s \quad (10)$$

$$d[\text{N}_2\text{O} + \text{N}_2]_g/dt = K_{23} [\text{NO}_3^-]_s \quad (11)$$

The assumption of first order kinetics was validated by the data obtained from controlled batch reactor experiments for nitrification, denitrification, mineralization and immobilization (Mehran and Tanji 1974). Under most field conditions where concentration of substrate is neither limiting nor in excess, the assumption of first order kinetics appears to be valid.

Initial and Boundary Conditions

The following provides a set of general initial and boundary conditions:

$$C(x,z,0) = C_0(x,z,0)$$

$$C(x,z,t) = C \text{ on } A_1 \times t[0,\infty)$$

(Dirichlet boundary condition or first kind)

$$\begin{aligned} & -(\Theta D_{xx} (\partial C/\partial x) + \Theta D_{xz} (\partial C/\partial z) - q_x C)n_x - (\Theta D_{zx} (\partial C/\partial x) + \Theta D_{zz} (\partial C/\partial z) \\ & - q_z C) \cdot n_z \\ & = Q(x,z,t) + (q_x n_x + q_z n_z)C(x,z,t) \text{ on } A_2 \times t[0,\infty) \end{aligned}$$

(Neumann boundary condition or second kind)

$$\begin{aligned} & -(\Theta D_{xx} (\partial C/\partial x) + \Theta D_{xz} (\partial C/\partial z) - q_x C) \cdot n_x - (\Theta D_{zx} (\partial C/\partial x) + \Theta D_{zz} (\partial C/\partial z) \\ & - q_z C) \cdot n_z = Q(x,z,t) + (q_x n_x + q_z n_z)C(x,z,t) \text{ on } A_3 \times t[0,\infty) \end{aligned}$$

(12)

(Cauchy boundary condition or third type)

METHODS OF SOLUTION

The transport equations, applied to the vadose zone and the aquifer, are solved by finite difference and finite element methods, respectively. Although the primary reason for this approach lies in the chronological development of the computer codes, the advantages of the approach are numerous and, therefore, it can be justified. The finite difference method of solving equations (1) and (5) for the vadose zone, where biophysicochemical processes are numerous and complex but geometry is one-dimensional and simple, has the advantage of being computationally efficient. On the other hand, the finite element method is suited for the aquifer where the only mechanism of transport is dispersion-convection but the transport is two-dimensional and geometry is more complex.

The finite difference scheme describing the transport of water and N in the vadose zone forms a computer code called "UCD-RANN". First, the water flow portion of the code solves eq. (1) and stores on tape the values of water content, velocity and water uptake, for each time step. Once the flow field is defined, the N transport portion of the code calculates the distribution of soluble N species.

The finite element scheme forms a complete code called "FLOWS" which solves equations (1) and (5) for water and solutes in two dimensions (Noorishad and Mehran 1982). This code first solves the water flow for the aquifer, and through an auxiliary finite element routine calculates velocities at the nodal points of the elements. Then, the code solves the transport problem using the previously calculated velocities. The sequence of computational steps is shown in figure 2.

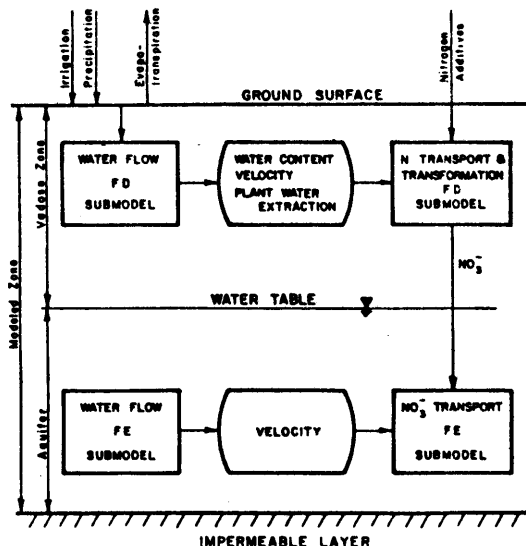


Fig. 2. Schematic diagram of the overall computational steps.

ILLUSTRATIVE SIMULATIONS

The main thrust of this paper is the idea of linking two powerful modeling techniques to provide an efficient and economical approach to solve the aquifer pollution problems. For this reason, the need for solving a sophisticated hypothetical problem was not warranted. Furthermore, simulation of realistic field problems requires considerable amount of support not available to the authors at this time. Therefore, to demonstrate the capability of the model in predicting the distribution of nitrates in the vadose zone and the underlying aquifer system, a simple hypothetical problem is considered. The schematic diagram of the flow region is shown in figure 3.

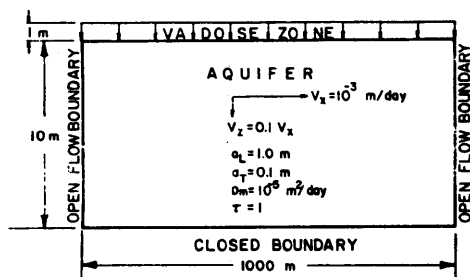


Fig. 3. Geometry of the modeled zone.

Modeling of the Vadose Zone

The vadose zone is assumed to be 1 m thick with a uniform volumetric water content of 0.3 percent. It is also assumed that a steady vertical Darcy velocity of 0.1 m/day is sustained throughout the problem time. The initial concentrations of NH_4^+ and NO_3^- are assumed to be 100 and 10 mg/liter, respectively. The dispersion coefficients for NH_4^+ and NO_3^- are calculated from eq. (7) using $D_m = 7 \times 10^{-5} \text{ m}^2/\text{day}$, and $a_L = 0.03 \text{ m}$ (Biggar and Nielsen, 1976). In the hypothetical problem presented here, the assumptions of small thickness of the vadose zone and relatively large areal extent of the flow region are satisfied.

To illustrate the capability of the model, the processes of nitrification and plant uptake are considered. To demonstrate the effect of nitrification, a rate of $K_{12} = 0.2 \text{ day}^{-1}$ for the entire vadose zone is assumed. The concentration profiles of NH_4^+ and NO_3^- at an elapsed time of 2.5 days are shown in figure 4. In this simulation, it is assumed that there is no plant uptake and no other N transformations present in the system. As shown in figure 4, the nitrate concentration at the bottom of the vadose zone is approximately 45 mg/liter which is the upper limit for drinking water standard set by the U.S. Public Health Service. The effect of plant uptake of NH_4^+ and NO_3^- on concentration profiles is also shown in figure 4. For this simulation a constant plant water extraction of $W(z,t) = 0.2 \text{ cm}^3 \text{ cm}^{-3}$ per day for the entire vadose zone is assumed.

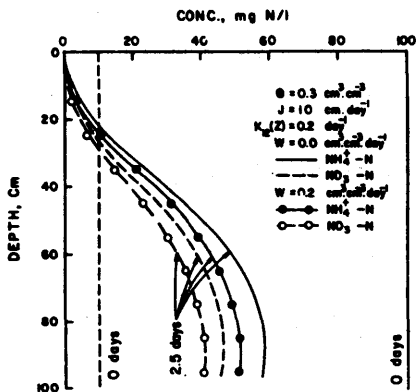


Fig. 4. Concentration profiles of mobile N species in a soil column leached with N-free water demonstrating the effect of nitrification and plant uptake.

Long term intensive agricultural practices may produce leachates of high nitrate concentration much in excess of U.S. Public Health standards (45 mg/liter). However, convection-dispersion phenomena in the aquifer may be sufficient to dilute the concentration to acceptable levels for groundwater to be used as a drinking water supply. Therefore, the impact of large-scale agricultural activities on groundwater contamination can be evaluated only if a quantitative assessment of transport in the vadose zone and the aquifer can be made.

The flux of water and nitrate below the root zone is in a continuous change and always lags the imposed conditions (on the vadose zone) by the order of months or years (Nielsen et al. 1980). However, for the purpose of demonstrating the capability of modeling of the aquifer, it is assumed that agricultural activities have reached a steady state in which the nitrate concentration of the leachate is 45 mg/liter.

Modeling of the Aquifer

The transport of the received leachates from the vadose zone is analyzed by means of the finite element portion of the modeling scheme in a vertical cross section of the aquifer. The aquifer is assumed to be 1,000 m long and 10 m thick. It is also assumed that the aquifer has a natural gradient of 1/1,000 and hydraulic conductivity of 1 m/day. This leads to a horizontal velocity distribution of 10^{-3} m/day throughout the aquifer. To produce mixing by hydrodynamic dispersion in the vertical direction, in addition to molecular diffusion, a vertical component of velocity equal to 10 percent of horizontal velocity is assumed. Although this can be real in leaky aquifers, it is solely introduced here to demonstrate the vertical migration of contaminant. The geometry of the aquifer and the value of the parameters used in the simulation are shown in figure 3. A finite element mesh composed of 261 elements with 300 nodal points represented the region of interest in the computer simulations. A constant concentration input of 45 mg/liter of nitrate is imposed on the water table. The concentration profiles for the beginning (A), the middle (B) and the end (C) of the aquifer are shown in figure 5. The advancement of the front or the contaminated zones for various times are shown in figure 6. It can be observed that even under the assumption of favorable mixing conditions, the depth of the contaminated zones is not large even in the times of the order of decades. It is also observed that a rather small horizontal hydraulic gradient is sufficient to prevent any accumulation of the leachates.

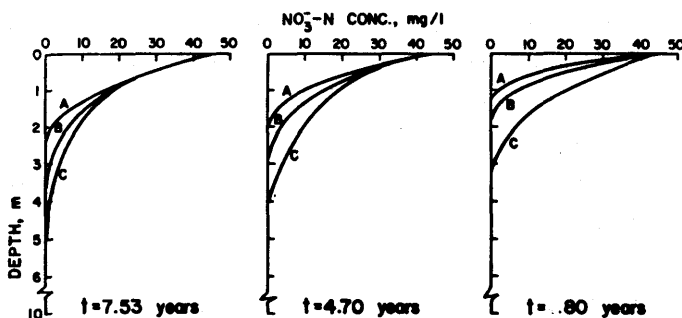


Fig. 5. Nitrate concentration profiles at sections A, B and C.

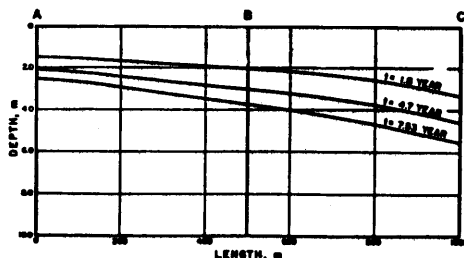


Fig. 6. Contaminated zones of the aquifer at various times.

CONCLUDING REMARKS

Investigations of aquifer pollution problems from surface sources require an integrated analysis of the vadose zone and the aquifer system. Application of numerical models to problems of large scale in time and space demands efficient solution approaches as well as sound conceptualization of physical phenomena. In the modeling concept presented here, we have taken advantage of two powerful and efficient modeling techniques incorporating the salient features of transport processes in the vadose zone and the aquifer system. A simple hypothetical simulation is presented to illustrate the concept.

It is believed that for problems of field scale, one-dimensional transport in the vadose zone with two-dimensional flow in the aquifer allows a realistic description of transport processes in the overall flow region. This type of modeling approach provides an efficient and practical tool for long-term prediction of the impact of agricultural activities on aquifer systems and evaluation of various management alternatives. Application of the model to actual field situations and evaluation of sensitivity of important parameters require considerable amount of support not available to the authors at the present time.

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FACTORS OF BACTERIA AND VIRUS TRANSPORT IN GROUNDWATER

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ABSTRACT

The underground transport of pathogenic bacteria and viruses may be described by the general transport equation considering dispersion, adsorption and biological elimination. The survival time of bacteria and viruses in groundwater is different for the specific species and for the specific groundwater environment. Dispersion causes a distribution of pollutants in time and space, thus their concentration decreases in time and with transport distance. Microorganisms are reversibly adsorbed on underground particles, which causes a retardation of their transport velocity with respect to groundwater flow velocity. An additional approach is provided by the filter theory.

INTRODUCTION

For the assessment of groundwater protection zones against pathogenic microorganisms (bacteria and viruses), the controlling mechanisms which must be studied are mainly:

- i) the persistence of bacteria and viruses under the biological and chemical conditions of the groundwater
- ii) the physical, physico-chemical and microbiological processes which control the transport of microorganisms in groundwater.

The most important pathogenic bacteria and viruses which might possibly be transported in groundwater flow are *Salmonella* sp., *Shigella* sp., *Yersinia enterocolitica*, *Y. pseudotuberculosis*, *leptospira* sp., *Francisella tularensis*, *Dyspepsia coli*, enterotoxigenic *E.coli* (ETEC), *Pseudomonades*, *Vibrio* sp., *Legionella* sp. and the viruses

infectious hepatitis virus, polio virus, coxsackie viruses, adenovirus, rotavirus, Norwalk-like virus (Gerba & Keswick, 1981). The groundwater may be contaminated by sewage containing the excrement of carriers or diseased persons. Using realistic data on the concentration of pathogenic bacteria and viruses in sewage, surface water and drinking water it can be concluded that the concentration of these microorganisms has to be diminished by 7 log units in potable water with respect to sewage water. This means that the 99.9% elimination of pathogenic microorganisms in groundwater that is broadly used as a measure for the effectiveness of the elimination processes, is not sufficient (Matthess & Pekdeger, 1981).

The sizing of groundwater protection zones are based on empiric observations of the elimination of microorganisms in groundwater. In Austria, Germany and the Netherlands, groundwater protection zones are established by calculating a flow time of 50-60 days to a well, a period which is considered to cover the survival time of pathogenic bacteria and viruses. In Switzerland, where physical and physico-chemical processes are more emphasized, the protection areas are calculated on the basis of ten days flow time or at least a flow path of 100 m length in porous media. For developing countries, 5-50 m are proposed (Lewis et al. 1981).

SURVIVAL OF BACTERIA AND VIRUSES IN GROUNDWATER

Two groups of microorganisms are to be differentiated when the survival of bacteria and viruses in groundwater are considered:

- i) allochthonic pathogenic microorganisms (parasitic bacteria and enterotoxine producing bacteria) which enter the groundwater due to contamination, and
- ii) autochthonic groundwater microorganisms.

The autochthonic microbial groundwater population flourishes under favorable ecological conditions, developing high population densities ($>>10^3/\text{ml}$). The allochthonic bacteria are usually eliminated in the groundwater environment, but under oligotrophic conditions they may survive without a substantial decrease or even have a slight increase in the germ number during the first 1-7 days.

After this period, the elimination of bacteria and viruses may be approximately described by an exponential function (Merkli, 1975, Berg, 1967).

$$C(t) = C_0 \exp(-\lambda(t-t_0)) \quad (1)$$

$t \geq t_0$ and $t_0 \geq 7$ days

$C_0, C(t)$ = initial concentration and concentration at time t

λ = elimination constant = $\ln 2 / (\tau_{1/2})$

t = time

$\tau_{1/2}$ = half-life (mostly between 1 and 20 days)

It follows from equation (1) that after a very rapid elimination at the beginning, bacteria and viruses may still exist in very small quantities in groundwater even after longer times (e.g. 6 months). The elimination constant depends on physical, chemical and biological parameters, and is specific for the different microbial species (Matthess & Pekdeger, 1981). Since it is not yet possible to predict with the necessary accuracy the elimination constants on the basis of controlling factors, they must be measured for each specific species and environment. The published values are contradictory and vary over a broad range (Fig. 1).

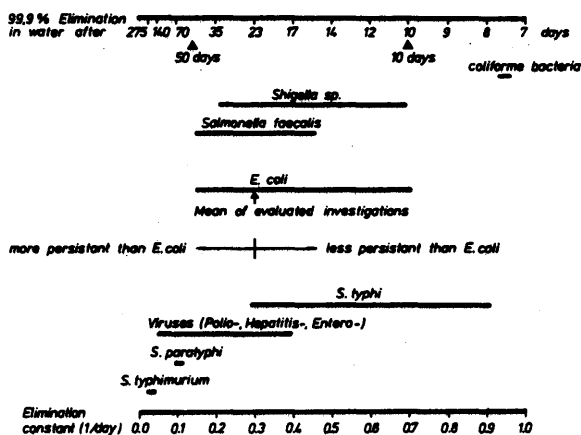


Fig. 1. Elimination constant and 99.9% elimination of some relevant bacteria and viruses in groundwater.

Elimination is a combined effect of the physical (temperature), biological and chemical conditions. The biological factors (bacteriophages, autochthonous parasitic bacteria, eg. *Bdellovibrio bacteriovorus* and protolytic bacteria) are the most important factors for the survival of pathogenic bacteria and viruses.

The published data on the elimination of bacteria and viruses in aquifers show that survival time cannot be the only criterion for the purifying effect of underground passage. Therefore, physico-chemical transport processes are to be considered.

TRANSPORT PROCESSES

Polluted groundwater plumes undergo dispersion, which causes a distribution of the pollutants in time and space so that in the contaminated groundwater body the concentration decreases in time and with transport distance.

These processes may be described by the general transport equation in vectorial form (Bear, 1972):

$$\delta C / \delta t = \text{div} \{ (D/R_d) \cdot \text{grad } C \} - (v_w/R_d) \cdot \text{grad } C - \lambda C \quad (2)$$

D = coefficient of hydrodynamic dispersion = $D' + D_d + D_e$

D' = coefficient of hydromechanic dispersion

D_d = diffusion coefficient

D_e = coefficient of active mobility of bacteria

$\text{grad } C$ = concentration gradient

v_w = average groundwater velocity

R_d = retardation factor

λ = elimination constant

The active mobility of the bacteria decreases with decreasing temperatures (e.g. for *E.coli* 0.1 m/d at 20°C).

The hydrodynamic coefficient D depends on the groundwater flow velocity.

$$D = \alpha \cdot v_w + b \quad (3)$$

The dispersivity coefficient α is a function of the inhomogeneity of the aquifer, thus α increases with the scale of the experiments. Porous media used in laboratory experiments have dispersivity coefficients in the order of 0.1 cm - 1 m; in field experiments in the order of 0.1 - 100 m, and in fissured and karstic rocks 10 - 1000 m (Matthess & Pekdeger, 1981). In fractured and karstic aquifers a "purification" of groundwater occurs due to dilution below detection level although the residence time in these aquifers may be too small for an effective elimination and the filtering qualities of these aquifers are generally poor.

The groundwater velocities in porous aquifers are usually less than one meter/day up to a few meters/day, velocities above 10m/day are restricted to very coarse sediments and high hydraulic gradients. In hard rock aquifers, the groundwater flow velocities are quoted to be between 0.3 m and 8000 m/day; in karstic aquifers up to 26,000 m/day. Therefore, it can be concluded that the propagation of pollutants in fractured and karstic aquifers is much faster than in porous aquifers.

The retardation factor describes the retardation of any pollutant with respect to groundwater (eq. 4).

$$R_d = v_w/v_m = 1 + (\rho_b / n) K_d \quad (4)$$

with the bulk density of the pollutant ρ_b , porosity n , the mean groundwater velocity v_w and the mean transport velocity of the microorganisms v_m . The empirical distribution coefficient K_d can be obtained by batch tests in the laboratory. In diluted suspensions K_d is equal to the coefficient of the Freundlich' isotherm, which

defines the equilibrium between the concentration of the suspended (C_s) and adsorbed (C_a) microorganisms (eq.5).

$$C_a = K_d C_s^n \quad (5)$$

The constants K and n are assumed to be specific for the investigated aquifer and microorganisms. The adsorption of viruses and bacteria takes place quite rapidly (2h and 24h respectively). There is little information on desorption velocity.

In field experiments, retardation factors between 1 and 2 are found for bacteria (*E.coli* and *Serratia marcescens*). The viruses in general, especially the polio viruses, have very high K_d -values (up to 500), depending on water properties and the properties of the respective virus.

Thus, underground movement can provide a very effective protection against virus contamination. However the viruses can be desorbed again, when cation concentrations decrease (e.g. due to a very intensive rainfall), thus being enabled to travel further (Duboise et al., 1976).

Bacteria can attach themselves actively and irreversibly on the surface of the solid aquifer materials. The attached bacteria are protected against other influences and find higher nutrient concentrations, which decreases the elimination rate. Attachment is most intensive in the phase of exponential growth. Attachment may be of importance immediately after the intrusion of polluted water.

FILTRATION PROCESSES

Elimination is a complex process. It includes the time-dependent elimination described by eq 1. Furthermore, elimination dependent on the length of flow path can be observed, which may be explained with the help of filtration theory.

Microorganism transport may be limited by the pore size and the size

of the microorganism. Because of this, mechanical filtration processes in gravelly aquifers cannot be very effective due to the small diameters of bacteria ($0.2 - 5 \mu m$) and viruses ($0.25 - 0.02 \mu m$). For the bacteria mechanical filtration should be expected below the grain size of coarse loam with uniform grain size distribution. In natural sediments with heterogeneous grain size distribution some percentage of the pore diameters can interfere with bacteria transport ($> 10\%$ in sand) (Matthess & Pekdeger, 1981).

Particle accumulation on solid substance surfaces is affected by sedimentation, flow processes, diffusion and interception as shown in fig. 2.

YAO et al. (1971) give the following equations (6)-(10)

$$\ln (C/C_o) = - (3/2) (1-n) \alpha \eta (L/d) \quad (6)$$

$$\eta = \eta_D + \eta_I + \eta_G \quad (7)$$

$$\eta_D = 4.04 P_e^{-2/3} = 0.9 (kT / \mu d_p d v_f)^{2/3} \quad (8)$$

$$\eta_I = (3/2) (d_p/d)^2 \quad (9)$$

$$\eta_G = (\rho_p - \rho) g d_p^2 / 18 \mu v_f \quad (10)$$

with C_o, C = influent and effluent concentration

n = porosity

α = stabilization coefficient

η = single collector efficiency

d = grain size of filter material

d_p = diameter of suspended particles

L = bed depth

η_D, η_I, η_G = single collector efficiency for diffusion, interception, sedimentation

P_e = PECLET number

k = BOLTZMANN' constant

T	= absolute temperature
μ	= water viscosity (dynamic)
v_f	= filter velocity
ρ_p, ρ	= density of suspended particles and water
g	= gravity constant

The importance of sedimentation for bacteria and viruses has been apparently overestimated in the past; sedimentation is very important for the accumulation of inorganic mineral suspension (density about $2,5 \text{ g/cm}^3$), but not for microorganisms (particle size less than $5 \mu\text{m}$, density about 1 g/cm^3). For particles with diameters of less than $1 \mu\text{m}$ (e.g. viruses), diffusion is very important. Its effectivity increases with decreasing particle size. As seen in figure 2, filtration processes have their minimum impact at a particle size of about $1\text{--}5 \mu\text{m}$, which corresponds to the size of most bacteria.

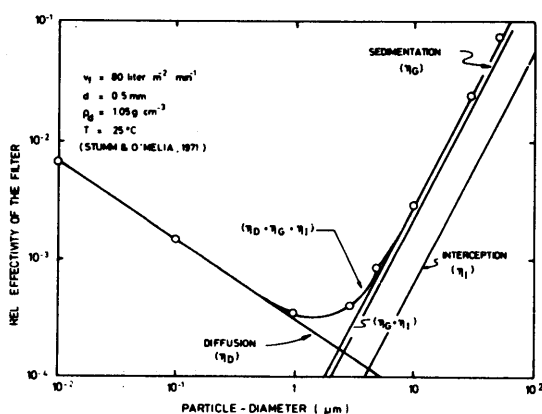


Fig. 2. Mechanisms of the filtration processes (YAO et al., 1971)

Recent studies in our institute comparing filtration of clay minerals ($< 2 \mu\text{m}$ fraction) with that of the bacteria, show that bacteria are held back more effectively than clay minerals. This is contradictory to the prediction derived from eq. (6) - (10). Although the calculations for clay mineral filtration agree reasonably with the experimental results, the bacterial elimination is better than calculated.

The reason for this effect is presumably the active mobility of bacteria. Although the active velocity of bacteria (> 0.1 m/d) is not very important with respect to the groundwater velocity, it should be very effective in intergranular voids with small pore diameters in the transportation of bacteria to the surface of underground particles. Thus, the single collector efficiency will be much higher than calculated. The main transport processes for bacteria are the random "tumbling" and the systematic chemotactic motion (Maeda et al., 1976).

The solid particles of an aquifer are usually negatively charged. An exception are the iron and manganese hydroxides and organic substances at low pH-values. The generally negatively charged bacteria and viruses are strongly adsorbed by anionic adsorbents, and only slightly by cationic adsorbents. The negatively charged particles stay in suspension in sand filters, as the repulsive electrostatical forces are stronger than the Van der Waals forces. Dissolved cations in water decrease the repulsive forces of the grain surfaces. Monovalent cations are adsorbed by solid substances and decrease their charge deficiency. Under these conditions, mass forces are more effective and an accumulation of particles can take place. This can be demonstrated by the dependence of virus adsorption on the solute concentration of the water and also for bacteria (Gerba & Keswick, 1981; Duboise et al., 1976). Bivalent cations can also cause a positive charge deficiency so that the electrostatic forces can be more efficient for bacteria and virus adsorption.

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MODELING NITROGEN BEHAVIOR IN THE SOIL PROFILE

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ABSTRACT

Three mathematical models (I, II and III) were developed to predict the transport and transformation of nitrogen in the soil profile. Model I is based on steady soil water flow whereas Models II and III are based on transient water flow. Model III is similar to Model II except that the dispersion term of the N equations was ignored. Model II provided best predictions whereas Model III proved to be inferior in comparison to Models I and II.

INTRODUCTION

The purpose of this paper is to present three mathematical models which were developed to predict the transport, transformations and plant uptake of N in the soil system. These models widely vary in their degree of complexity, method of solution as well as the computer time required for simulation. The need to predict the behavior of N in the soil-plant environment is essential in order to quantify N use by crops and leaching to the groundwater. Several mathematical models have been recently developed in order to describe the fate of N in the soil system. For an overview of the current models, the reader may refer to Nielsen and MacDonald (1978), Frissel and Van Veen (1980) and Iskandar (1981).

Most N models consider N transport and transformations under steady water flow in the soil profile. Although such models may not adequately describe N behavior in the dynamic root zone, they could be considered adequate under conditions of quasi-steady state in the lower portion of the soil profile. In general such models are simpler

in comparison to N models for transient water flow and require considerably less computer time. In contrast, N models which consider transient flow in unsaturated soils are more realistic since they simulate actual field condition of infiltration, redistribution and evaporation in the soil matrix. A number of these models have been recently introduced. The main disadvantage of such models lies in their complexity as well as the large number of soil parameter needed.

MATHEMATICAL ANALYSIS

In all three models described in this study, N transformation processes considered were: nitrification of NH_4^+ to NO_3^- , denitrification of NO_3^- and ion exchange of NH_4^+ . The nitrification and denitrification processes were considered of the first-order kinetic type where k_1 and k_2 (hr^{-1}) are the rate coefficients for nitrification and denitrification, respectively.

The ion exchange of NH_4^+ was assumed to follow a Freundlich equilibrium type reaction. A distribution coefficient K_D ($\text{cm}^3 \text{g}^{-1}$) was used to describe the equilibrium process between the NH_4^+ in the soil solution and that on the exchange sites. It should be noted that the organic-N phase was not included in these models, i.e. N mineralization and immobilization processes were ignored.

Model I

In this model, N transport and transformations was considered under conditions of steady state water flow. In addition within each distinct soil layer in the profile, uniform soil water content was assumed. Therefore, the NH_4^+ and NO_3^- transport and transformation equations may be written as (Selim 1978)

$$\partial C / \partial t = D \partial^2 C / \partial z^2 - v \partial C / \partial z - (\rho / \theta) \partial S / \partial t - k_1 C - q_1 \bar{\theta} \quad (1)$$

$$\partial Y / \partial t = D \partial^2 Y / \partial z^2 - v \partial Y / \partial z + k_1 C - k_2 Y - q_2 \bar{\theta} \quad (2)$$

where C = concentration of NH_4^+ in soil solution ($\mu \text{ g/cm}^3$)
 Y = concentration of NO_3^- in soil solution ($\mu \text{ g/cm}^3$)
 D = solute dispersion coefficient (cm^2/hr)
 v = pore-water velocity (cm/hr)
 $\bar{\theta}$ = soil water content (cm^3/cm^3)
 ρ = soil bulk density (g/cm^3)
 S = amount of NH_4^+ sorbed ($\mu \text{ g/g}$)
 q_1 and q_2 = rate of NH_4 and NO_3 uptake ($\mu \text{ g/cm}^3 \text{ hr}$).

In the above two equations, the parameters D , v , ρ , $\bar{\theta}$, k_1 and k_2 are considered constant for a uniform soil profile. For layered soil profiles, these parameters must be provided for each soil layer in the profile (see Selim, 1978). The NH_4^+ ion exchange process was considered as a linear Freundlich type,

$$S = K_D C \text{ or } \partial S / \partial t = K_D \partial C / \partial t \quad (3)$$

The terms q_1 and q_2 represent plant uptake (sink) terms for NH_4^+ and NO_3^- , respectively. The approach used here was the Michaelis-Menton macroscopic type where N uptake was considered a function of root density and N concentration in soil solution,

$$q_1 = R(z,t) C I_{\max} / (K_m + C + Y) \quad (4)$$

$$q_2 = R(z,t) Y I_{\max} / (K_m + C + Y) \quad (5)$$

where $R(z,t)$ is the root distribution or length (cm) as a function of soil depth and time, I_{\max} is the maximum rate of uptake per unit root length ($\mu \text{ g/hr cm}$) and K_m is the Michaelis constant ($\mu \text{ g/ml}$). For further details on the uptake (sink) term the reader may refer to Selim and Iskandar (1981).

The explicit-implicit finite difference method was used in solving eqs. 1 and 2. The solution was stable and a mass balance was maintained as a check on the numerical results.

Model II

In this model, soil water flow conditions were unsteady or transient where the water flux and soil water content are considered as variables with time and depth. Under transient water flow, the transport and transformation equations for NH_4^+ and NO_3^- can be written as (Selim and Iskandar, 1981)

$$\partial (\Theta C) / \partial t = (\partial / \partial z) (\Theta D \partial C / \partial z) - \partial (vC) / \partial z - \rho \partial S / \partial t - k_1 \Theta C - q_1 \quad (6)$$

$$\partial (\Theta Y) / \partial t = (\partial / \partial z) (\Theta D \partial Y / \partial z) - \partial (vY) / \partial z + k_1 \Theta C - k_2 Y - q_2 \quad (7)$$

where Θ is the soil water content (cm^3/cm^3), v the water velocity or Darcy's flux (cm/hr) and the remaining parameters are similar to those described under Model I (Eq. 1 and 2). Moreover, the transformation rate coefficients k_1 and k_2 were considered variable in order to account for the effect of the soil environment (such as pH, temperature, suction, etc.). Therefore,

$$k_1 = F_1 \lambda_1 \quad (8)$$

$$k_2 = F_2 \lambda_2 \quad (9)$$

where F_1 and F_2 are empirical functions which vary between 0 and unity and λ_1 and λ_2 are maximum rate coefficients. In Model II, it is necessary to describe the water flow conditions prior to solving the N Eq. (6) and (7). The water flow equation, commonly known as Richard's equation, modified to account for water uptake may be written as

$$c(h) \partial h / \partial t = (\partial / \partial z) (K(h) \partial h / \partial z) - \partial K(h) / \partial z - A(z, t) \quad (10)$$

where h = soil water pressure head (cm)

$c(h)$ = soil water capacity, $\partial \Theta / \partial h$ (cm^{-1})

$K(h)$ = soil hydraulic conductivity

$A(z, t)$ = rate of water uptake by plants ($\text{cm}^3/\text{hr cm}^3$)

In Eq. (10) the water capacity term is obtained from the soil water content-pressure head relationship. The plant uptake $A(z,t)$ term was described by a macroscopic approach as a function of root density and soil water hydraulic conductivity,

$$A(z,t) = ETR(z,t)K(h) / \int_0^l R(z,t)K(h)dz$$

where ET is the rate of evapotranspiration (cm/hr) and l is the maximum root penetration in the soil profile (cm). Richard's flow Eq. (10) and the N Eq. (6) and (7) were simultaneously solved, subject to the appropriate boundary and initial conditions using the explicit-implicit numerical method. The stability and convergence criteria are discussed in Selim and Iskandar (1981).

Model III

This model is similar to Model II and describes N behavior for unsteady transient water flow in the soil. However, several simplifying assumptions were introduced. The dispersion term D in eq. (6) and (7) were ignored. Such an assumption is primarily based on the fact that the convective or mass flow term is primarily responsible for solute transport whereas the dispersion term influences to a great extent the shape of the breakthrough curve of a solute. Moreover, the method of solution for the N equations were that of the explicit finite difference method. These assumptions provided not only computer time savings but simplified the model considerably. Accordingly, the NH_4^+ and NO_3^- equations used in Model III were

$$\partial \partial C / \partial t = v \partial C / \partial z - k_1 \Theta C - \rho \partial S / \partial t - q_1 \quad (11)$$

$$\partial \partial Y / \partial t = - \partial Y / \partial z + k_1 \Theta C - k_2 \Theta Y - q_2 \quad (12)$$

where, similar to Model II, both v and Θ were considered variables. The water flow (eq. 10) was also incorporated in Model III and was solved using the explicit-implicit method. For further details on Model III see Selim (1980).

MODEL EVALUATIONS

As discussed earlier, Model I does not consider transient water flow. However, knowledge of the soil water regime is essential in order to arrive at realistic values for the soil water parameters required in Model I. Specifically, average water flow velocity and soil water content are needed. It is also necessary to account for the evapotranspiration rate when estimates for an average water velocity are made. None of these difficulties are encountered in the use of Models II and III since both models consider transient and soil-unsaturated water flow.

The three models presented here were evaluated using experimental data from a greenhouse study using soil lysimeters by Iskandar and Selim (1981). The lysimeters, were instrumented at several soil depths and received frequent applications of wastewater. The wastewater was applied at a rate of 3.83 cm twice weekly (at 3 or 4 day intervals). Two soils were used, a Windsor sandy loam and a Charlton silt loam. For each soil, the total profile length was 150 cm. with A, B and C horizons 15, 30 and 105 cm. thick, respectively. A mixture of grasses were grown on each soil and total N uptake by plants was measured over a 5-month period.

Concentration of N in the applied wastewater varied between 17 to 29 $\mu\text{g/ml}$ for NH_4^+ and zero to 29 $\mu\text{g/ml}$ for NO_3^- . Soil solution samples were collected at several soil depths and analyzed for NH_4^+ and NO_3^- concentrations. In this study, the models were evaluated utilizing the experimental data from the Charlton soil only.

On the basis of Model II validation, as discussed in Iskandar and Selim (1981), the values chosen for λ_2 , K_m and I_{\max} were $0.01 \text{ (hr}^{-1}\text{)}$, $1.0 \text{ (}\mu\text{g/ml)}$ and $5 \times 10^{-4} \text{ (}\mu\text{g/hr. cm)}$, respectively.

Also, the functions used for F_1 and F_2 (Eqs. 8 and 9) were assumed to be dependent on θ and h only. In arriving at best predictions for Models II and III for transient water flow, the water flow equation was validated prior to incorporation with the N equations. Water flow predictions showed (see Iskandar and Selim, 1981) good agreement with experimental data for both Windsor and Charlton soils. The data base used were suction data at several soil depths for wastewater applica-

tion cycles and from gravimetric moisture determinations. The soil water properties for individual soil layers are given by Iskandar and Selim (1981). In addition an exponential decay function was used to describe the root density with soil depth and a constant value for ET of 0.5 cm/day was used in the model and was calculated from the water balance from several waste water cycles.

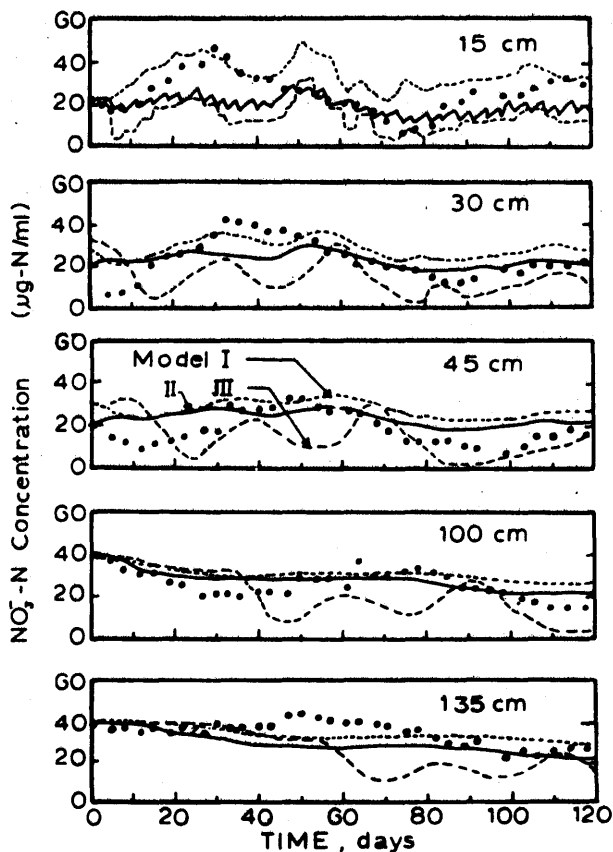


Fig. 1. Experimental and calculated NO_3^- concentrations for several soil depths for Charlton soil ($k_1 = 0.025 \text{ hr}^{-1}$ for model I, $\lambda_1 = 0.05 \text{ hr}^{-1}$ for models II and III).

In arriving at N prediction using Model III it was assumed that the flow velocity throughout the soil profile equals the amount of water applied minus evapotranspiration. This simulated a continuous and constant input within each wastewater application. The concentration of NH_4^+ and NO_3^- in the applied wastewater were also considered constant and were adjusted for evapotranspiration.

Moreover, an average moisture content for each soil layer was calculated on the basis of experimental data.

Predicted and experimental results of the NO_3^- concentration with time for several soil depths are shown in Figs. 1 and 2. In Fig. 1 the K_D value used was $1.5 \text{ cm}^3/\text{g}$ for all three models. The nitrification coefficient k_1 for Model III was chosen as 0.025 hr^{-1} which was considered constant. Whereas, for Models II and III, k_1 was considered as a variable (see eq. 8) depending on soil water suctions where λ_1 was chosen as 0.05 hr^{-1} . It should be noted here that these values are similar since F_1 was estimated to be approximately 0.5 for this soil (Iskandar and Selim, 1981). In Fig. 2, the K_D value used was $2.5 \text{ cm}^3/\text{g}$ where λ_1 was 0.075^{-1} for Models II and III and k_1 of 0.05 hr^{-1} for Model I. Although none of the calculated provided close agreements with experimental data for all depths and over the 120-day period, it is clear that Model III is far more inferior than the comprehensive Model II or the steady water flow Model I. Moreover, it appears that Model I provided best agreement at lower soil depth (100 and 135 cm).

This is expected since in this soil water content and velocity changes during infiltration and redistribution occurred primarily in the top portion of the soil profile. In general, Model II provided better predictions than the other two models. Predicted and experimental results of cumulative N uptake is shown in Fig. 4. These results indicate that the predictions of N vs time were linear for all three models.

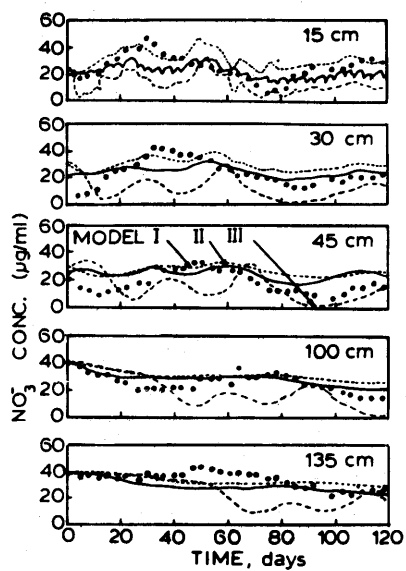


Fig. 2. Same as Fig. 1 except k_1 and λ_1 were 0.05 and 0.075, respectively.

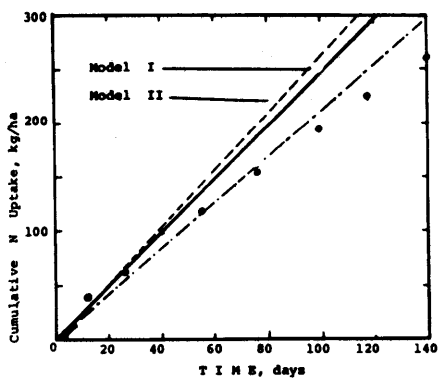


Fig. 3. Experimental and simulated N uptake for Charlton soil.

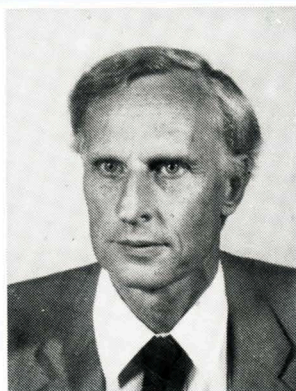
It is surprising, however, that the steady water flow Model I provided closer agreement for plant uptake of N in comparison with the other two models. Finally, it should be emphasized that for the simulations shown, Model I required 17.7 seconds CPU time, using IBM 370/3033. In contrast, Models II and III required 4.4 and 2.8 minutes, respectively.

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