Solid Waste: Assessment, Monitoring and Remediation
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III.3

Agrochemicals: transport potential in the vadose and saturated zones

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III.3.1. Introduction

Modern agriculture became successful mainly due to the use of pesticides and fertilizers. Fertilizers contain large amounts of nitrogen, phosphorus and potassium associated with chloride, sodium and sulfate.

Earlier, pesticides had contained copper, mercury and arsenic salts. These caused damage to the soil structure and texture and the soil organisms, some of which can still be detected. In the 1960s, a transition to organic substances was made that had the effect of pesticides. These new substances are degradable and are formulated so that they when applied provide the wanted optimal effect.

Agrochemicals must be available for uptake by plants, i.e. must be sorbed on the plant itself or on solids, such as organic substances and clays. Once there, they are also subject to different types of chemical–microbiological reactions and can thus change their bonding and their health effects. They are also subject to different transport processes as solutes or fixed on particles through overland discharge, interflow and groundwater recharge. In between retardation, chemical–microbiological reactions and transport, conflicts of interest can build up that depend mainly on the weather conditions and are generally difficult to solve. For example, although the local precipitation should be known, it cannot be forecasted with the necessary accuracy either on a long or on a short term for any specific locality. Therefore, agricultural activities cannot be adapted to weather conditions to minimize the input of agrochemicals on water resources.

The way in which the agrochemicals are applied affects their availability for crops and neighboring compartments, like the atmosphere and the hydrosphere.

- In the agricultural fields, damage can occur to the soil organisms or the physical properties of the soil or
- Unwanted accumulations of the agrochemicals can develop in the plants.
- Trace gases (N_2O, CH_4, H_2S) emitted into the atmosphere can initiate unwanted chemical reactions and
- Pollutants (substances in unwanted concentration) such as eutrophying and toxic substances can enter the hydrosphere.

Though introduced to the environment in purpose, overdosed agrochemicals not utilized in accordance with the aim should be treated as wastes. Substantial amounts of residual agrochemicals are also disposed with packaging waste.

III.3.2. Pesticides in agriculture

In Germany, approximately 2000 pesticide compounds and around 300 active ingredients are approved for use; 80% are applied in agriculture. The pesticide market in Germany rose in the three decades from 1970s to 1990s from 10,000 to 30,000 t/a (Amann et al., 1989) or *ca.* 2.5 kg/(ha a) have been applied, as an average, in agriculture. Meanwhile, the amounts applied have fallen to 0.5–1 kg/(ha a). If it was assumed that the pesticides do not react during the underground passage, an infiltration of 200 mm/a of water produced pesticide concentrations of 1.3 and 0.3 mg/l in groundwater, respectively.

According to the Drinking Water Ordinance of the European Community, water used as drinking water may contain only 0.1 μg/l of any single active ingredient and a sum of 0.5 μg/l for all active ingredients. There are different reasons for this low limit:

- Pesticides are not natural products and therefore should not be in groundwater at all.
- The effects that pesticides might have upon health and life are inadequately known.
- Of the metabolites of the pesticides, less than 15% are known and there are indications that the toxicity of the metabolites could be even stronger than the mother substance itself and, simultaneously, the mobility of the metabolites increases mostly with decreasing molecular weight.

At the time when the limits were set for pesticides allowed in groundwater, the detection limit was fixed. The same procedure today could lead to lower limits.

The theoretical, maximum discharge of agricultural pesticides of 1.3 mg/l to groundwater and the limit of 0.0001 mg/l for drinking water show the high requirements that must be placed upon the pesticides with respect to:

- the intensity and rate of the sorption onto organic and inorganic particles,
- their decay with respect to the water flow underground and
- the metabolites produced and their mobility and toxicity.

These requirements, however, have been only partially fulfilled for optimal drinking water protection.

Most of the publications have dealt with the behavior of pesticides in soils (Edwards, 1966; Harris, 1969; Hayes, 1970; Adams, 1973; Haque and Freed, 1972; Führ and Mittelstaedt, 1979; Hellig and Gish, 1986) and only a few focused on the fate of pesticides in subsurface waters. Furthermore, most of the experimental investigations were conducted on a small scale (small-scale lysimeters, microcosms) (Bergström, 1990; Dickopf, 1994; Dörfler et al., 1994) and only a few have been performed relative to the field scale (Dickopf, 1994). Thus, the knowledge available concerning the behavior of pesticides in compartments adjoining the soil is limited. Yet it is known that in most middle and coarse grained aquifers and in fissured aquifers, there are high pesticide concentrations in groundwater. This contamination of the groundwater is still rising. Therefore, extensive efforts have been made, to gain a better understanding of:

- the retention capacity of soils for pesticides,
- the decay kinetics and the decay products of pesticides by applying ^{14}C-labeled substances and

- the propagation behavior of pesticides with and without bonding onto particles in the vadose (unsaturated) zone and aquifers.

III.3.2.1. Types of pesticides and their sorption onto solids in the soil

Preferentially, the pesticides applied today in agriculture belong to triazines, urea derivatives, phenoxy carboxylic acids, chlorinated hydrocarbons and carbamates. Lately, heavy metal sulfates have also been in use again. About 62% of the pesticides are applied as herbicides, 24% as fungicides and 7% as insecticides. The remainder refers to other applications. *Circa* 75% of the total amount of fungicides are applied in vineyards and *ca.* 75% of all herbicides are used in corn and grain fields. In using these pesticides, the timing of the application, relative to the growth stage of the plant and relative to the weather conditions, is decisive as to how effective and whether they will be transported by discharge into the adjacent compartments.

Above all, pesticides are adsorbed on the humates and clay minerals, which are predominantly abundant in the A- and B-horizons of the soil (Fig. III.3.1); both of these horizons are thin in temperate climates. In the non-weathered rock below these, adsorbents are mostly not as important for the sorption of pesticides; either they have been mechanically filtered (Seiler, 1988; Matthess et al., 1991; Klotz, 1994) or, as in the case of the humates, are subject to microbiological decay.

Most of the organic pesticides are subject to slow sorption kinetics on humic substances and clay minerals and develop a very strong binding on the humates. This leads in hilly terrains

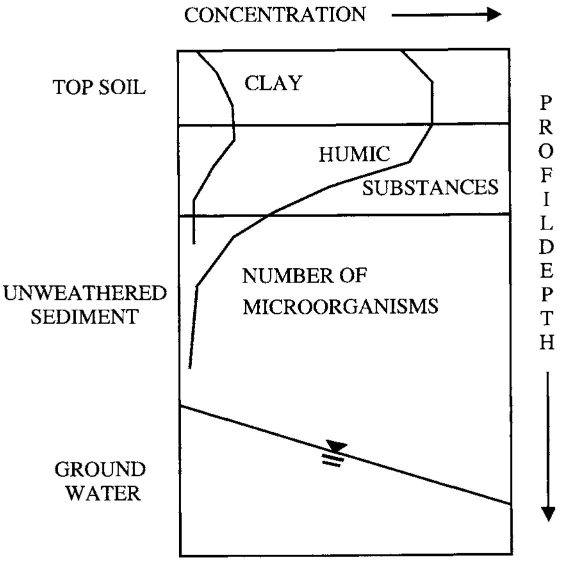

Figure III.3.1. Distribution of clay, organic substances and organisms in soil and unweathered rock.

- under groundwater recharge conditions with flow velocities of a few meters per year to a quasi-complete sorption and
- under bypass-flow velocities of a few decimeters to meters per day (see below and Chapter V.2.2), however, to a rapid transport of the pesticides out of the soil zone into the sediments with weak sorption properties or to surface water resources.

Sorption of pesticides is an important prerequisite for microbiologic degradation. This decay is especially efficient in biofilms that are in aquifers rather thin (less than a few tens of micrometers) and cover the particle's surface in soils, less in the unsaturated and the saturated zones. These biofilms contain a sufficiently high and specialized microbiologic community for pesticide degradation. Recent investigations show that below the soil zone there may develop a microbiological population, which could also cause such degradation (Dickopf, 1994; Seiler et al., 1996). Yet it requires an incubation period, to adapt to the changes in the chemical composition of subsurface water, which is much longer in the unsaturated than in the saturated zone. As to what degree of change and at which maximal concentrations this response is possible are not yet known.

The slow sorption of pesticides onto surfaces can be considerably disturbed by discharges as a consequence of precipitation. In hilly terrain, the precipitation producing discharges is spited at the land surface into overland discharge and the infiltration of seepage water. This seepage water is further divided into the fast bypass-flow, turning mostly into lateral flow, and the slow groundwater recharge. Such bypass-flow can make up 25–50% of the seepage water infiltration in unconsolidated sediments and mostly covers 40–50% in consolidated rocks. As a result, the discharge consists of two components with high (overland discharge and bypass-flow) and one component with slow flow velocities (groundwater recharge). Bypass-flow and overland discharge act opposite to a complete sorption of pesticides, if they were applied shortly before the precipitation event, and may transport pesticides as well as metabolites out of the soil. In contrast, the slow movement of the groundwater recharge favors the sorption of pesticides underground.

The high flow velocities of overland flow (several hundred meters per day) and interflow (from 0.5 m/d to several meters per day) also favor the transport of particles such as dissolved organic carbon (DOC) colloids and clay minerals, which can both have accretions of pesticides. However, the subsurface transport of clay minerals is generally less important than that of DOC, because clay minerals form very slowly as compared to DOC. The pool of DOC always has a better regeneration capability than that of the clay minerals and the particle sizes of the DOC are generally smaller than that of the clay minerals. Therefore, due to the existing pore size distribution in the sediments and in the soil, a total or selective retention of the large clay and only a partial retention of the small, colloidal particles take place (Matthess et al., 1991).

Due to the aforementioned and the generation of discharge in landscapes, it follows that after precipitation periods on hilly terrains, shock loads of pesticides repeatedly discharge (Fig. III.3.2). This occurs during the periods when agricultural pesticides are applied, as they are partially dissolved and partially bound to particles. Yet, even long after the pesticides were applied, such shock loads in surface waters can be clearly detected (Fig. III.3.2); at these times particle transport prevails.

The stated, particle favored run-off transport of pesticides into rivers and lakes decreases the pesticide concentration in the soil and thus reduces the direct input into

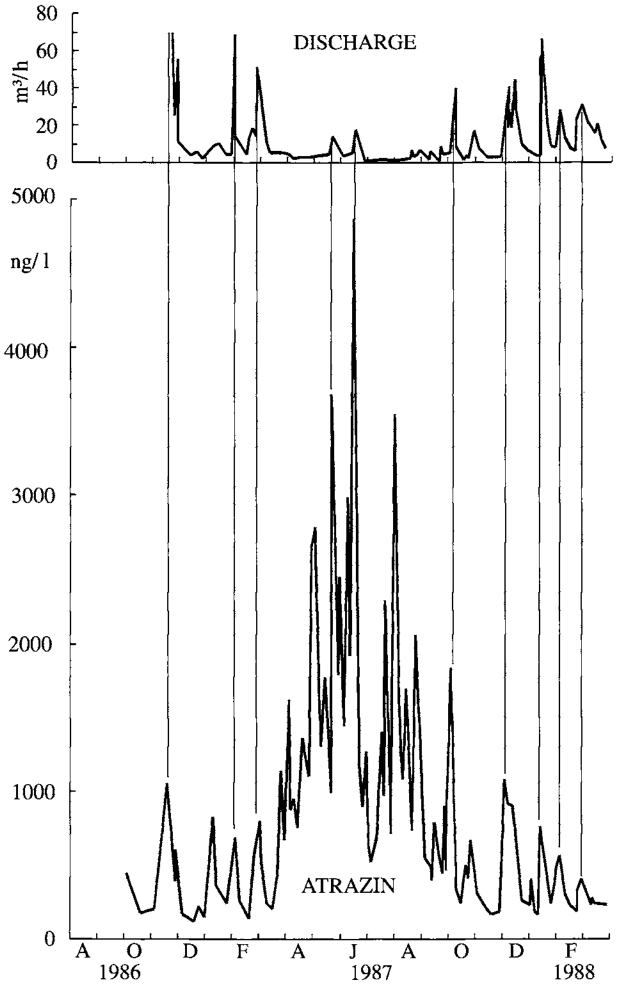

Figure III.3.2. Atrazine in the discharge of an upland stream.

the groundwater. However, the shock loads may re-enter the groundwater recharged, e.g. by bank filtration, if the surface water was not previously treated.

Batch laboratory tests consistently show that the sorption onto montmorillonites and illites is pesticide specific and much lower at neutral and basic pH values than at acidic pH ranges (Fig. III.3.3); only lindane is sometimes accreted onto montmorillonites at neutral pH values. For DOC, the sorption is almost the same at basic, neutral and acidic pH ranges (over pH 4), and becomes even stronger onto clay minerals.

An example for the migration of terbutylazine in subsurface waters with and without humates is shown in Figure III.3.4, as a result of laboratory tests (Dörfler et al., 1994); in this case, the flow velocities of the terbutylazine, which is involved in particle flow, are higher as compared to dissolved pesticides.

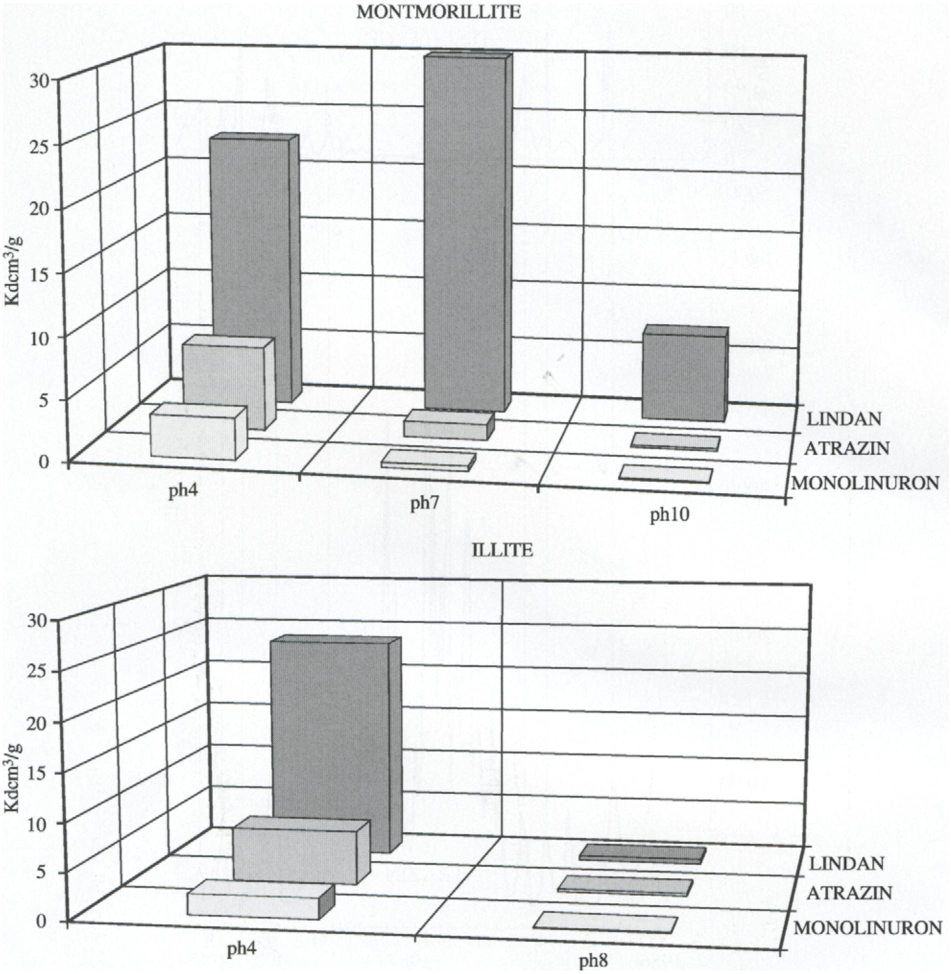

Figure III.3.3. Sorption of selected pesticides onto montmorillonite and illite at different pH values (Dickopf, 1994).

III.3.2.2. Migration of pesticides in the vadose and water saturated zone

Laboratory tests on the transport of pesticides (Dickopf, 1994; Klotz et al., 1995), in particular of atrazine, terbutylazine, lindane, diuron and monolinuron show that atrazine migrates in almost all sediments practically as fast as the water itself; its behavior is to a large extent independent of the hydraulic conductivity, the flow velocities and the compactness of the soil and sediment; all the other pesticides mentioned above show in laboratory experiments slower propagation velocities as compared to water flow with increasing:

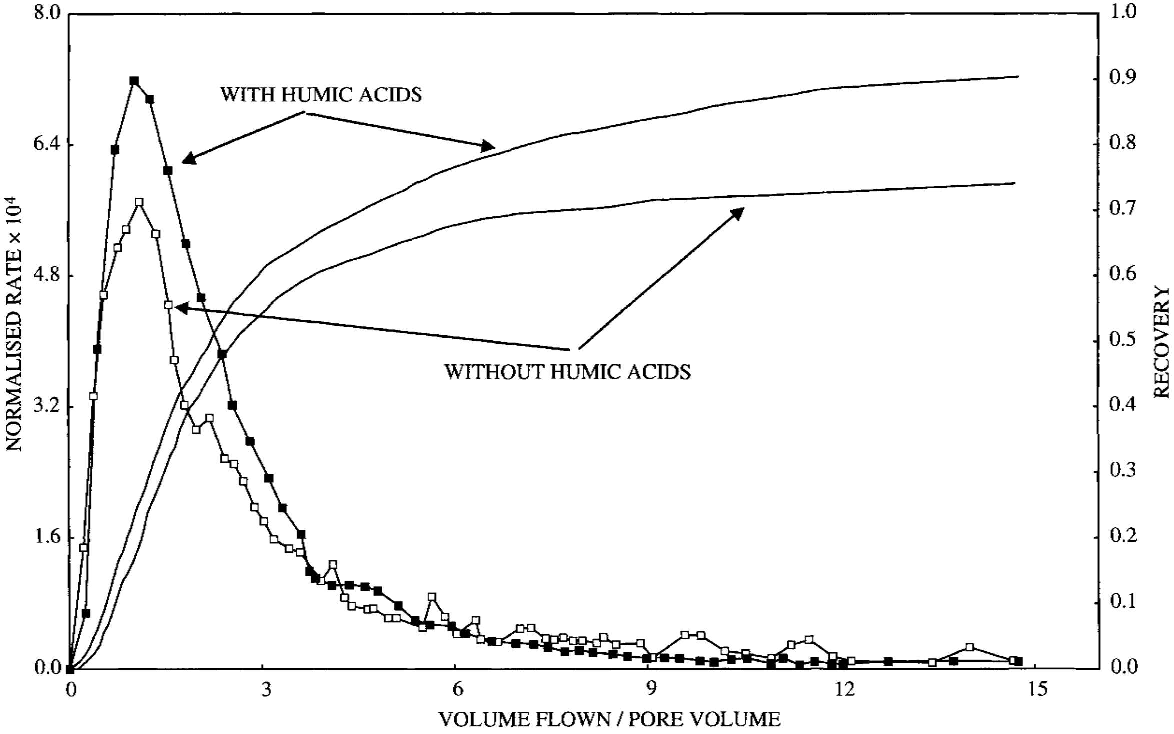

Figure III.3.4. Migration of terbutylazine with and without humates (Klotz et al., 1995).

- organic carbon contents in the sediments, since then the sorption increases,
- application quantities, since then the solubility is exceeded,
- compactness of the sediments and clay contents, since both increase the specific surface responsible for sorption processes,
- biomass fractions, which increase the incorporation in the biomass or the development of biofilms and
- with decreasing water contents and flow velocities, since then mechanical retention increases and sorption processes with slow kinetics quantitatively occur.

Examples for the influence of the effective flow velocity in the same aquifers (Quaternary gravels of the Munich Gravel Plain) upon the propagation velocities of different pesticides are shown in Table III.3.1 and Figure III.3.5. These field tests (Table III.3.1) were conducted without withdrawing groundwater, at effective flow velocities of 37 m/d and flow distances of 10 and 20 m with atrazine, lindane, monolinuron, diuron and a commercial atrazine, Gesaprim. As a non-reactive reference tracer, fluorescein was applied in parallel tests. In all the tests, no retardation of the pesticides was recorded, i.e. they seem to migrate as fast as the non-reactive tracer. Within the scope of the measurement accuracy, the total injected amount of the active ingredients was recovered (Seiler et al., 1995). In parallel laboratory tests on the same Quaternary gravel but flow velocities of only 3 m/d, the tests showed that migration of atrazine was not delayed with respect to the non-reactive reference tracer (tritium). Diuron, monolinuron, and to an even larger extent, lindane, all showed a flow retardation (Fig. III.3.5). These results demonstrate why a large range of retardation factors and K_D-values for most of the pesticides is reported. In order to create a better base for comparison, all indicated retardation factors required an exact description of the hydraulic boundary conditions and of sorption kinetics to which they refer.

Table III.3.1. Calculated recovery and retardation of selected pesticides in field tests in the Quaternary gravels of Dornach (Germany). The non-reactive reference tracer is fluorescein.

Pesticide	Flow path (m)	Recovery in % of the injection	Retardation
Atrazine	10	121	1.02
	20	104	1.02
Lindane	10	108	1.02
	20	48	1.02
Monolinuron	10	117	0.98
	20	104	1.00
Diuron	10	101	1.00
	20	96	0.99
Gesaprim	10	94	1.04
	20	97	1.00

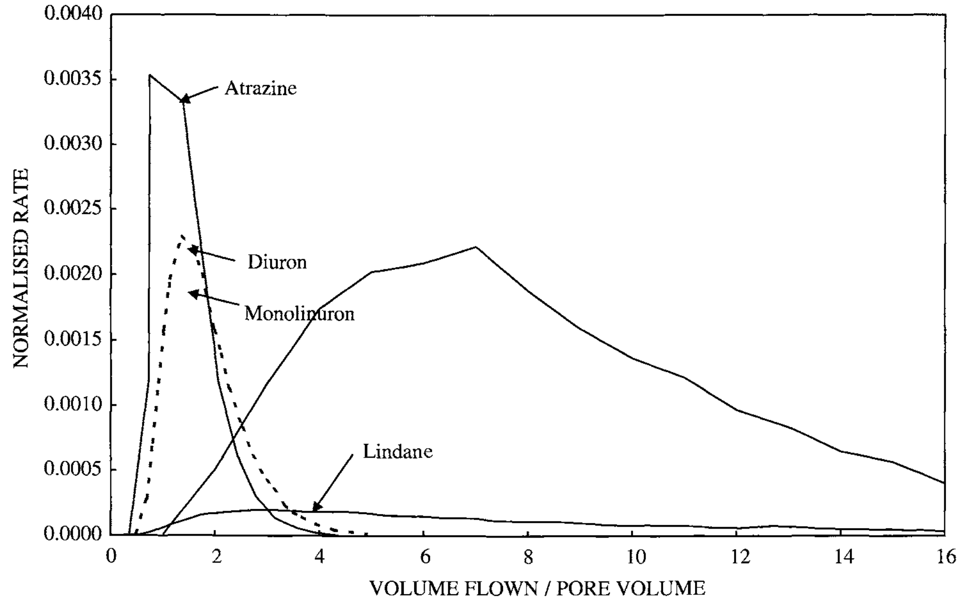

Figure III.3.5. Breakthrough curves for atrazine, diuron, monolinuron and lindane in Quaternary gravels. Laboratory tests; flow velocity 3 m/d (Dickopf, 1994).

III.3.2.2.1. Microbiological degradation of pesticides

The low concentrations of organic substances, the oligotrophy of the subsurface water in the sediments below the soil (Fig. III.3.1) and the primarily low microbiological population density of the solid surfaces lead to a decreased microbiological degradation of the pesticides in the vadose and the saturated zone. Another factor that can decrease the microbiological degradation efficiency is the low temperature of the underground water.

The mean underground temperature varies around the value of the mean annual air temperature; the amplitude of the seasonal temperature variations decreases with increasing observation depth and the phase shift of the temperature variations increases too (Fig. III.3.6). The neutral zone, below which in temperate climates noteworthy seasonal temperature variations of $\pm 0.1°C$ do not occur any more, is at 15–20 m below ground (Fig. III.3.6).

Generally, the degradation of pesticides can be described by first-order kinetics; in this case the half-life is a suitable measure for the mathematical description of the pesticide degradation.

The literature lists a large number of times for the half-life for pesticide degradation (Börner, 1967; Kohnen et al., 1975; Hamaker and Goring, 1976; Attaway et al., 1982; Scheunert, 1992); they cover a large range for most pesticides. This has different causes:

- It is not always sufficiently differentiated between mineralization (total degradation) and metabolization (partial degradation).
- A lack of data as to the degree of the metabolization achieved, which is sometimes even not possible to determine exactly without tracing the pesticide.

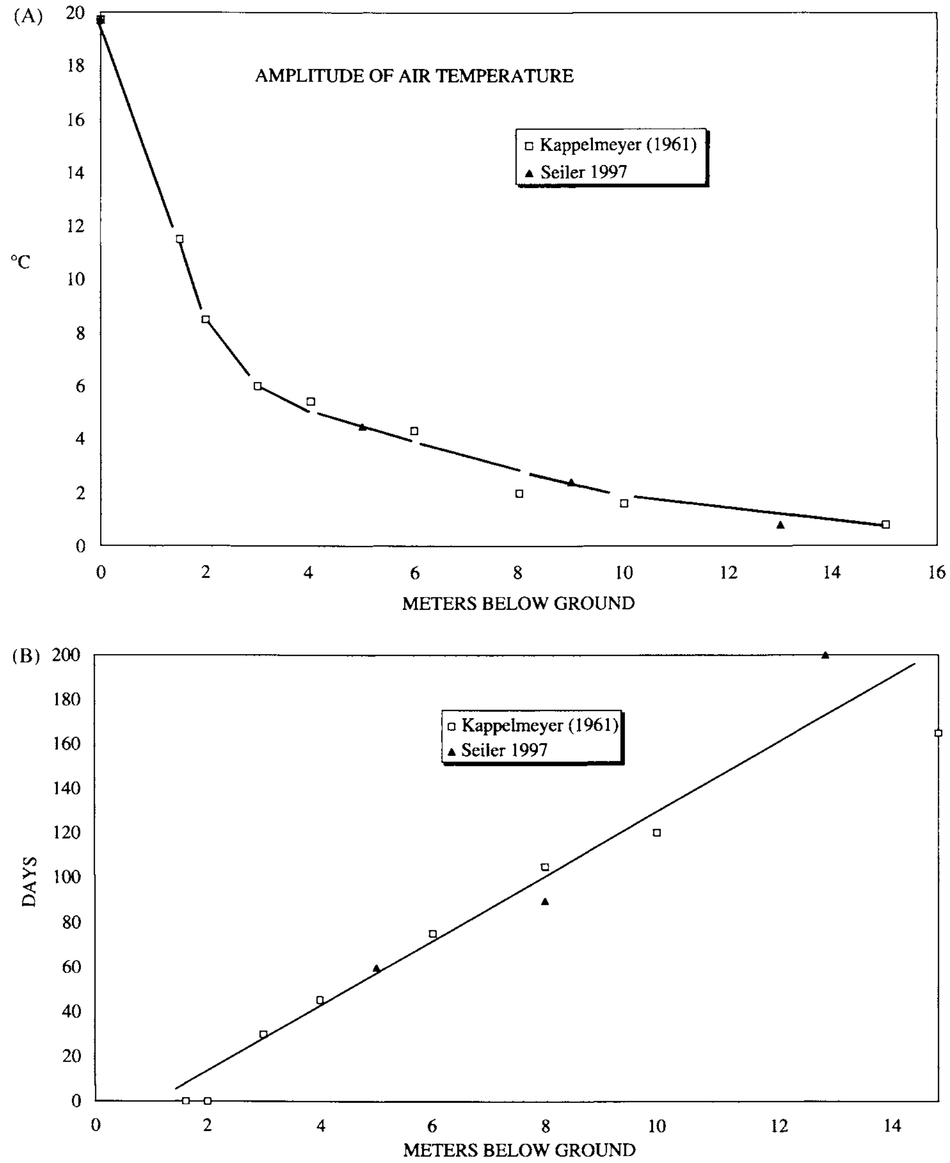

Figure III.3.6. Variations in the amplitude (A) and the phase displacement of the temperatures (B) in different depths below the ground surface as compared to the annual changes of the air temperature 1 m above the surface.

- The pH, temperature and environmental conditions under which the degradation experiment has been conducted, were different and frequently not well enough reported to allow reliable comparisons.
- Co-dissolved substances in the water may stimulate the metabolism.

- The influence of the relationship of the solution volume (*V*) to the sediment mass (*m*) upon the speed of the degradation processes is not taken into account.

The *V*/*m* ratio in batch experiments can strongly influence the experimentally determined value of the half-life for the pesticide degradation. Investigations with ethyl-parathion in a mix of Quaternary gravels (*m*) and carbonate groundwater (*V*) showed (Klotz et al., 1995) that the half-life decreases parallel to the *V*/*m* ratio (column curve in Figure III.3.7). In nature, the *V*/*m* ratio would be in the range of 0.1–0.15 cm^3/g, i.e. the half-life for the degradation of the ethyl-parathion would be extrapolated to about 10 days (Fig. III.3.7). In comparison, the half-life of the pesticide degradation in column tests (Figure III.3.7) is higher; here, the sorption kinetics relative to the flow velocity of the water plays a co-determining role.

How different the degradation behavior of the pesticides under different biotic, oxic and temperature conditions can be, can be instanced in several examples (Dickopf, 1994). However, these examples cannot be readily qualitatively or quantitatively transferred to other pesticides or even to those from the same substance family:

- Lindane has a much quicker degradation in oxygen-poor than in oxygen-rich environments (Fig. III.3.8).
- Atrazine is decomposed at practically the same slow rate whether or not the sediment and water have been subjected to sterilization.
- Pesticides from the same group behave differently under different degradation temperatures (Fig. III.3.9).

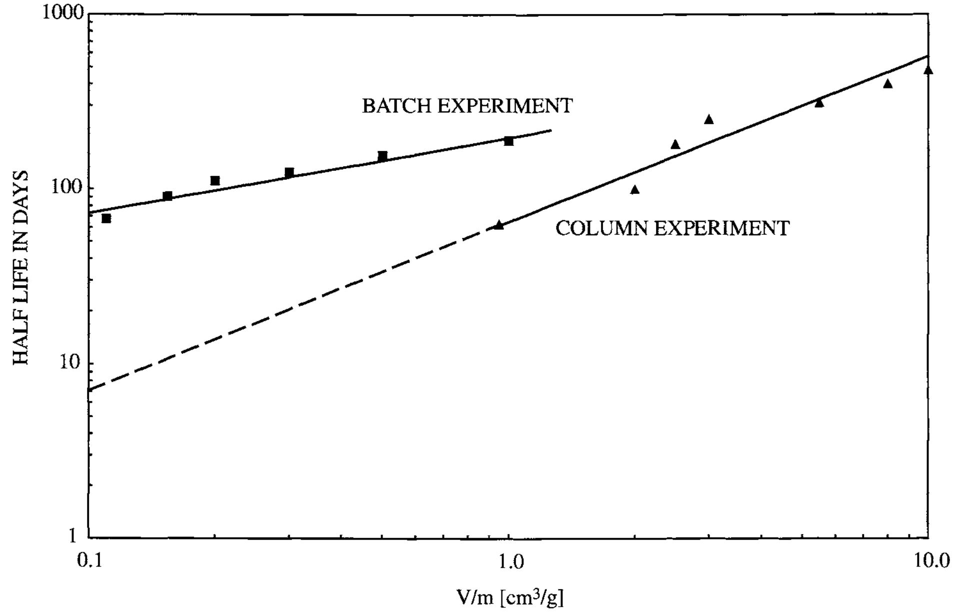

Figure III.3.7. Decrease of half-life of ethyl parathion vs. decreasing cumulative water loading, i.e. ratio of water volumes (*V*) to sediment mass (*m*) (Klotz et al., 1995).

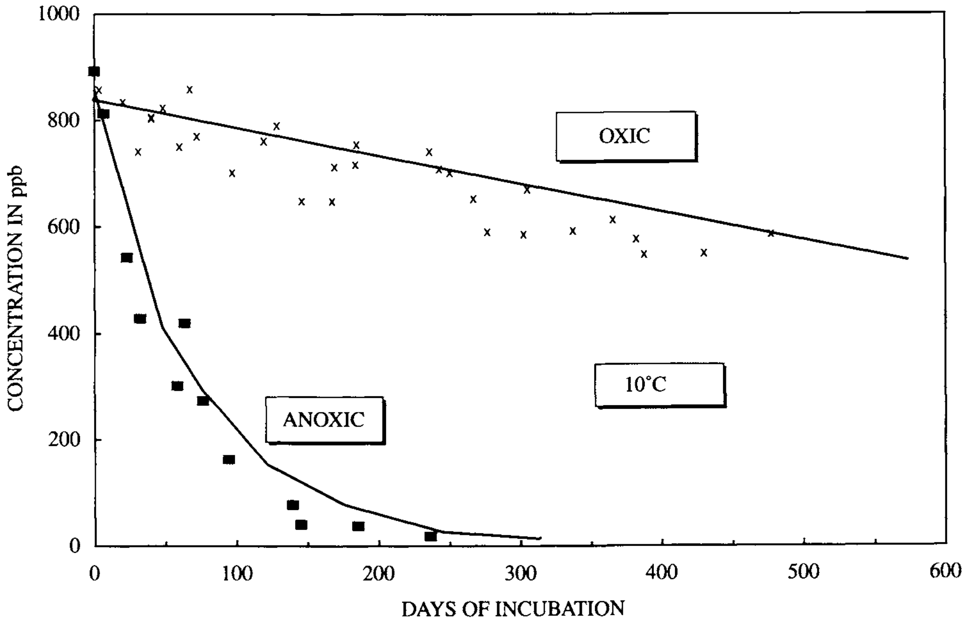

Figure III.3.8. The degradation of lindane under oxic and anoxic conditions (Dickopf, 1994).

Furthermore, degradation tests have shown that, e.g. nitrate- and sulfate-contaminated groundwater can bring about a higher degradation efficiency of the pesticides than uncontaminated groundwater (Fig. III.3.10).

There are still great uncertainties in the quantitative behavior of the pesticides and their impact upon the soil organisms. Due to this lack of understanding about the processes concerning most of the degradations, no reliable guidelines for the application of these substances can be formulated generally and mathematical calculations of the exposition of the pesticides in landscapes result in only rough estimates.

III.3.3. Nitrogen in agriculture

Nitrogen amounts to

4×10^{15} t in the atmosphere,
2×10^{15} t in the lithosphere,
1×10^{10} t in the hydrosphere,
5×10^{12} t in soils.

On the earth, annually 10–100 billion tons of biomass decomposes; thereby, nitrogen forms as ammonium and other compounds. At low oxidation numbers, nitrogen is strongly sorbed onto clay minerals and organic substances, at middle oxidation numbers it is volatile and at high oxidation numbers it is very water soluble. The volatile forms of nitrogen develop mainly during reduction processes

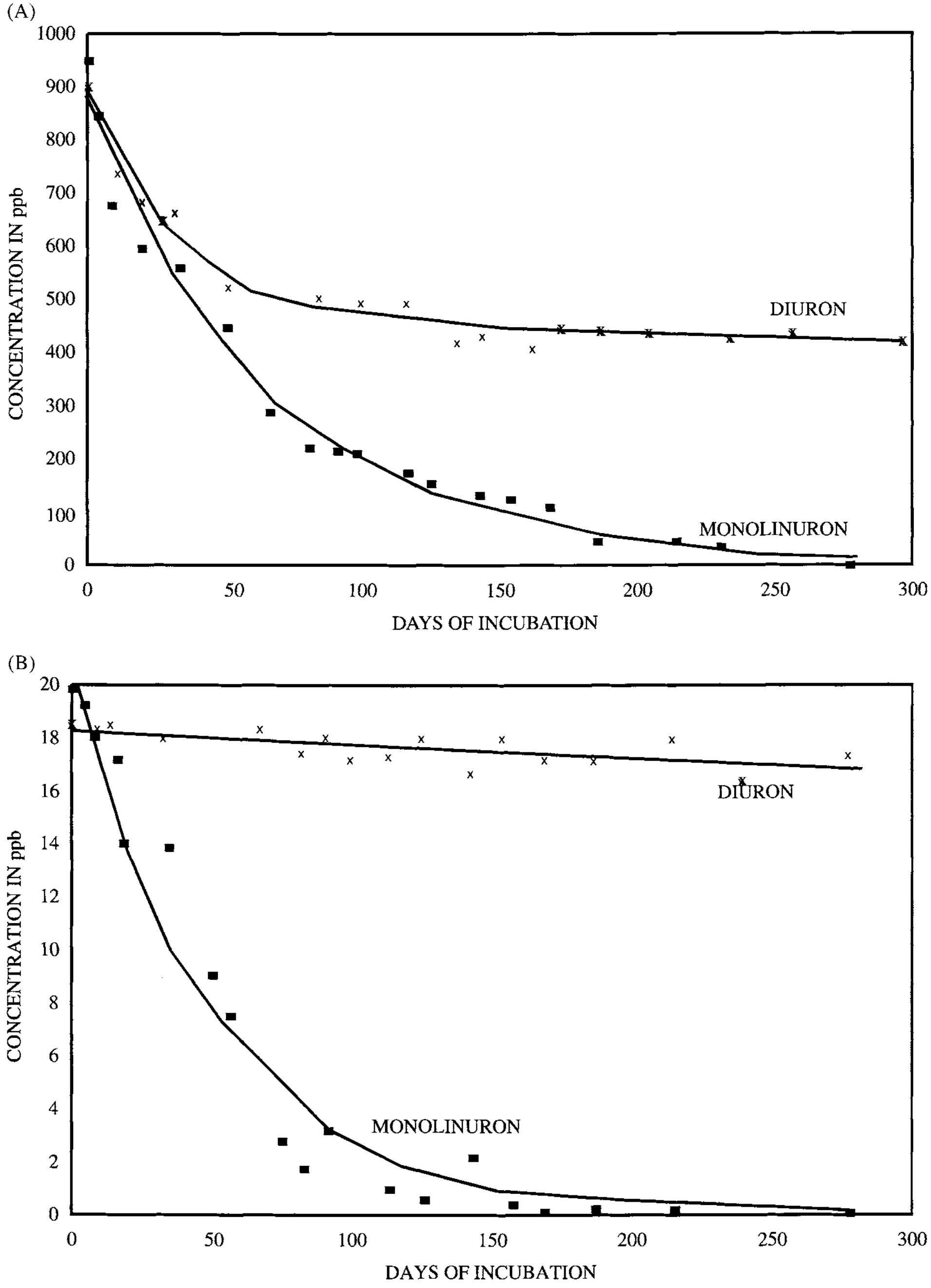

Figure III.3.9. The degradation of diuron and monolinuron at 20°C (A) and 10°C (B) (Dickopf, 1994).

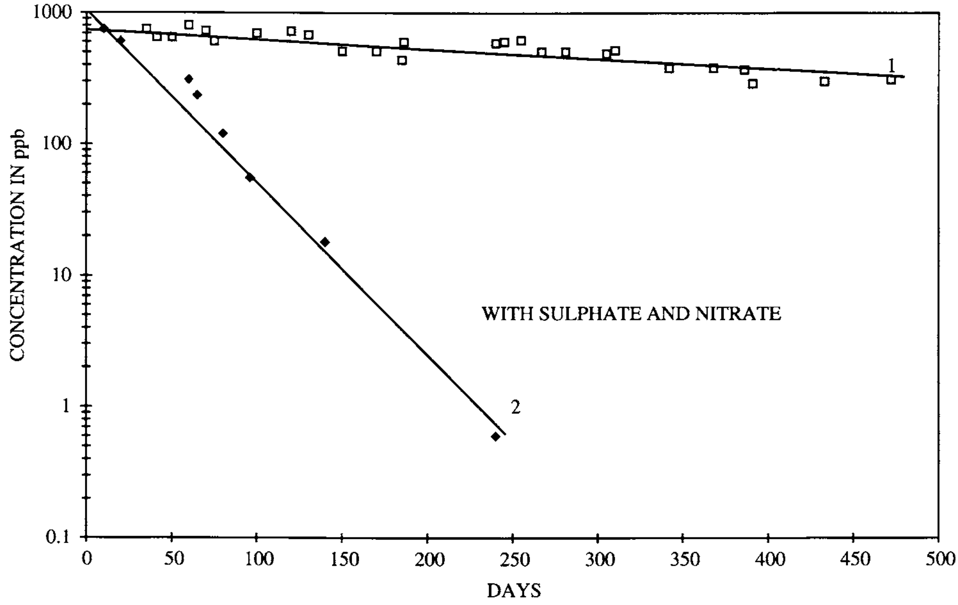

Figure III.3.10. The degradation of lindane in groundwater with normal chemical composition (top curve) and with elevated sulfate and nitrate concentrations (Dickopf, 1994).

such as denitrification; during oxidation processes such as nitrification or ammonification, this happens less. The volatile fraction of nitrogen can reach up to 15% of the inorganic nitrogen in the soil.

The natural nitrogen supply is not sufficient for the plant growth required in modern agriculture and thus, nitrogen as well as other nutrients must be added. Depending on the soil type, cultivation history and crop grown, currently, up to 255 kg/(ha a) of nitrogen are applied to agricultural crops; the natural decomposition of the organic substances in the soil and the nitrogen input from precipitation provide all together only *ca.* 15 kg/(ha a).

However, the oxidation and reduction processes that take place in this nitrogen pool in soil and underlying rock also produce unwanted release of material to the atmosphere as well as affecting water resources, life and health. These processes are microbiologically catalyzed and thus occur especially intensively in rocks and weathered formations with sufficient organic substance or sulfur in reduced form (pyrite).

During reduction processes such as denitrification, the trace gas N_2O forms, among others. This oxidizes to

$$2N_2O + O_2 \rightarrow 4NO \qquad \text{(III.3.1)}$$

In the presence of ozone, this reacts further to

$$3NO + O_3 \rightarrow 3NO_2 \qquad \text{(III.3.2)}$$

Nitrogen dioxide reacts then with atmospheric oxygen to

$$NO_2 + O \rightarrow NO + O_2 \qquad \text{(III.3.3)}$$

This reaction is favored by low temperatures and runs its course several times. If ozone and atmospheric oxygen occur together, ozone decomposes, but the nitrogen oxide contents do not change much over short and middle time periods. In contrast, oxidation processes produce nitrite and nitrate and both have high water solubility and can therefore enter the hydrosphere.

For infants and toddlers, excess in the total uptake of nitrate is responsible for the formation of nitrite, which can cause methemoglobinemia, resulting in an impairment of the oxygen uptake by the fetal red blood cells. The resulting cell damage can cause death. Adults can tolerate a higher nitrogen intake than infants and toddlers.

In determining the limits for the nitrogen uptake for people, the total nitrogen uptake through food and drink is essential: drinking water provides only a part of the total. In the European Community for the drinking water supply, the limit for nitrate is 50 mg/l, for nitrite 0.1 mg/l and for ammonium 0.5 mg/l. Long-term experience supports the validity of these limits that also contain a certain safety margin.

III.3.3.1. ***Average nitrogen input into the soil***

The natural, i.e. anthropogenically uninfluenced nitrogen input from the atmosphere into the soil is 7 kg/(ha a). With respect to the 200 mm/a of infiltration this amounts to 3.5 mg N/l, which corresponds to 15.5 mg/l NO_3^-. In addition to this natural nitrogen input, on the average, the same amount comes annually due to the mineralization of organic substances. This is essentially caused by microorganisms, is strongly temperature dependent and at optimum in the summer. These natural sources of nitrogen are superimposed on the input of synthetic fertilizers, from large-scale livestock farming, burning fossil fuels, industrial production plus sewage. It is estimated that besides a biologically produced nitrogen amount of 500 million tons/a, there is an additional amount of *ca.* 50 million tons/a due to technical processes.

In agriculture areas *ca.* 255 kg/(ha a) of natural and synthetic fertilizers are applied, whereby the synthetic fertilizers are responsible for more than half of this input. Considering the application of fertilizers over the last 100 years, it rose from 1880 to 1940 from almost none to about 90 kg/(ha a) and by 1980 to about 255 kg/(h a). With this, plant production was increased by a factor of 3–5.

Urban areas and roads produce a nitrogen input of 0.9 kg/(ha a); household sewage produces 11 kg/(ha a). Both essentially drain through the receiving streams and may lead, in areas where groundwater is supplied by riverbank filtration, to a potential ground- and drinking water burden.

Older statistics from the Federal Republic of Germany concerning nitrate contents in groundwater shows that 6.5% of the consumers were supplied with drinking water exceeding 50 mg/l of nitrate and 4.0% had drinking water with a nitrite content of over 0.1 mg/l. These values have a rising trend even today. Very high nitrate and nitrite contents occur frequently in areas with intensively farmed crops such as vineyards and vegetables.

III.3.3.2. Nitrogen leaching in soils

If nitrogen enters the soil as ammonium nitrogen, it is optimally sorbed onto humic substances and clay minerals and can only become mobile through oxidation to nitrite or nitrate. In the root zone of arable lands, however, the oxidation processes are hindered by the reducing environments in the vegetation period and the little bacterial oxidation of ammonium by *Nitrosomonas* and *Nitrobacter* in this environment. On the other hand, nitrate also gets denitrified. Thus, the species of the nitrogen input, the organic and mineralogical composition of the rock and the chemical environmental conditions in the soil determine the extent of the N-retention, N-release and N-availability to the plants. These ratios undergo changes:

- Due to nitrogen input from the atmosphere in high oxidation numbers, i.e. nitrogen enters the soil in a mobile form.
- By the type of agriculture; there are long periods in the year with no active root zone and thus a reduction zone is missing. At these times nitrification is dominant.
- Finally, to increase the productivity of the soil, intensive nitrogen fertilization is carried out, which leads to strong nitrate leaching into the groundwater under unfavorable weather and agriculture conditions.

The three main processes are superimposed over others that also favor today's situation of nitrogen leaching in the soil:

- Plowing the soil facilitates aeration and oxidation processes occasionally prevail.
- The strongest groundwater recharge occurs in the vegetation free period. This is valid for our climate where groundwater recharge is the strongest in the winter; it is also valid in the tropics, where in the rainy season the fields lie fallow and are planted at the end of the rainy season and before the dry season.
- Soils with the highest groundwater recharge have the lowest clay content and thus the lowest inorganic retention capacity for nitrogen in low oxidation numbers.

The lowest nitrogen leaching in the soil occurs in areas with evergreens and natural stocks (Table III.3.2). In areas where crop rotation is practiced, it is dependent upon

- the soil structure and texture,
- the amount of rain,
- the seasonal change of the infiltration and the crop grown.

Nitrogen leaching ranges:

- in podsols from 5 to 20 kg/ha,
- in brown soils from 50 to 90 kg/ha.

It is modified by the uptake of crop from the soil that accounts for:

- fruits about 70 kg/ha and
- sugar beets about 300 kg/ha.

Data on these influencing factors based on detailed, long-term lysimeter observations, are available from Limburger Hof near Ludwigshafen (Pfaff, 1963) and from Weihenstephan (Amberger, 1976), as well as from pilot investigations in

Table III.3.2. Land use-dependent average nitrogen release in the Federal Republic of Germany (Wolters, 1982).

Agriculturally used areas without grasslands	25 kg/(ha a)
Grasslands	2 kg/(ha a)
Forest	2 kg/(ha a)
Wetlands, moor	2 kg/(ha a)

Nordrhein-Westfalen (Obermann and Bundermann, 1982) and in Fuhrberger Feld (Strebel and Renger, 1982).

Unfertilized lysimeters with conventional agricultural crop rotation show that high amounts of precipitation leached nitrogen much more than low amounts of rain (Table III.3.3). Considering the same substrate, there is a lower N-leaching at low than at high pH values; in this case the high proton supply has an impact upon the microbiologic efficiency of nitrification.

These values can only be conditionally used to calculate the nitrate input to groundwater, as they were obtained from lysimeters, mostly with disturbed texture and structure of soils and substratum. However, it can be clearly seen that:

- Nitrogen leaching from soils is higher in areas with high precipitation than in drier ones.
- At times there can be higher nitrogen release from fine-grained soils than from coarse-grained soils.
- More nitrogen is leached from the soil with high pH values than from the soil with low pH values.

The fact that more nitrogen is leached out of the same soil type at higher precipitation sums is closely connected to the fact that increase in the amount of oxygen goes along with increase in the precipitation amount, and thus an oxidizing environment is created for the nitrifying bacteria. The same holds true with respect to the pH value.

Table III.3.3. Nitrogen leaching from different soils at different precipitation sums and pH values.

Precipitation (mm/a)	pH	N-release (kg/(ha a))				
		Coarse sand	Sand	Loam	Humic loam	Silty loam
850	6.4	50	–	–	–	–
	7.2	–	–	–	72.8	–
	6.8	–	–	–	–	73.6
570	4.1	–	22	–	–	–
	7.6	–	30	–	–	–
	4.4	–	–	18	–	–
	7.0	–	–	25	–	–

During nitrification of nitrogen, which is accelerated bacterially, ammonia reacts to nitrite in the first reaction step:

$$NH_3 + 1.5O_2 \rightarrow NO_2^- + H_2O + H^+ \qquad \text{(III.3.4)}$$

During the reaction, protons formation causes a drop in the pH value. However, microorganisms essential to this reaction (*Nitrosomonas*) cannot tolerate low pH values, so their activity would be limited. As ammonium is strongly sorbed, the corresponding mobility of the nitrogen is lacking in soils with high clay content; in coarse soils sorption is less important and the high seepage water velocities facilitate the proton export and thus the nitrification.

Generally, in Germany, more precipitation falls during the hydrological summer half-year than in the hydrological winter half-year. On the other hand, the evaporation in the hydrological summer half-year accounts for 2/3 to 3/4 of the annual evaporation, so that during the hydrological summer half-year less seepage occurs. As a consequence, nitrogen is stored in the hydrological summer half-year and gets mobile in the vegetation-free period.

Due to the nitrogen leaching in the hydrological winter half-year, there is a lack of nitrogen in the spring at the beginning of the vegetation period. In nature, this is not replenished until mineralization of the organic substances occurs; therefore, nitrogen fertilizers are applied mainly during this season. The soil though has also very low nitrogen retention at this time. As a result, there is a high loss of the nitrogen fertilizers into the seepage water during this season. The extent of these losses in the spring period depends upon the amount of nitrogen applied, but also upon the grain size of the sediment out of which the soil has developed (Table III.3.4).

Whether the nitrogen fertilizer is in the form of ammonium sulfate, calcium cyanamide, ammonium saltpeter or carbonate ammonium saltpeter is not particularly important.

The plant type may influence the nitrogen leaching since the plants can build up nitrogen deposits. Due to the environmental conditions in their root zone, the plants are also a deciding factor in the oxidation of the nitrogen to higher oxidation numbers.

Table III.3.4. Nitrogen application and release from two different soils (Pfaff, 1963).

N-fertilizer (kg/(ha a))	N-release (kg/(ha a))	
	Sand	Loam
Without	39	22
80	37	21
160	44	24
240	55	36
320	72	53

Depending on the soil use and plant type, the following retention series is given:

Fallow < vine < summer grains < winter grains < vegetables < root crops
< grassland

However, this series of decreasing mean nitrogen leaching cannot be used to determine the expected groundwater charge with nitrates without further information. Other effective mechanisms are also of importance, such as:

- the type and time of application of the fertilizers and the type of crop,
- current and previous land use, especially the distribution from evergreens to deciduous land use,
- nitrogen losses due to denitrification by microorganisms.

Either organic or inorganic fertilizer can be applied, the soil always sorptively retains the ammonium fertilization, as long as oxidizing conditions in the root zone do not prevail or occur through a high groundwater recharge. Such oxidizing conditions occur in fallow periods, in which the soil is thoroughly leached of $N-NO_3^-$ by infiltrating precipitation and thus in the spring more fertilizer must be applied. Farming with intercrops is advantageous, since the soil is always covered with vegetation and has oxidizing conditions in the root zone for only short periods. This practice reduces the applied nitrogen fertilizer and contributes to groundwater protection. According to the field studies, the $N-NO_3^-$ concentrations in the groundwater were only half as high at the crop cultivation with intercrops as without, although the cultivation with intercrops required a larger amount of fertilizer (*ca.* 300 kg N/(ha a)).

Frequently, manure is spread on the soil during the fall or on the snow in the winter. This way of fertilizing allows the complete nitrate load and fecal microorganisms to enter the groundwater during the snowmelt, while applying organic fertilizer after snowmelt or after the rainy season provides optimal plant growth conditions.

Besides nitrogen fertilizer application, a liming of the soil is often carried out to reduce the acid content of the soil. Similar considerations are being made for forests. However, it is known that Ca-fertilization causes an increased release of the N from the soil, i.e. favors nitrate leaching.

Plowing grasslands play an important role in nitrogen leaching. If meadows are changed to crop fields, considerable nitrogen leaching starts. This nitrogen had been retained in the root zone of the plants before and gets released after plowing.

In a recent study, Hellmeier (2001) demonstrated by analyzing soil solutions and discharges that only in the effective root zone (0–90 cm below the ground surface) significant variations of nitrate and chloride concentrations occurred, which were not associated with respective nitrate consumption by the plants. In the unsaturated (vadose) zone below only trends of decreasing nitrate concentrations were observed since the application of nitrate fertilizers was reduced according to the demand of the plants (Fig. III.3.11).

The concentration variations reported by Hellmeier (2001) were found to be caused by the wash-out from the effective root zone through interflow that apparently predominated in the effective root zone (Seiler et al., 2002). This was observed in loess, as well as in sandy soils and sediments.

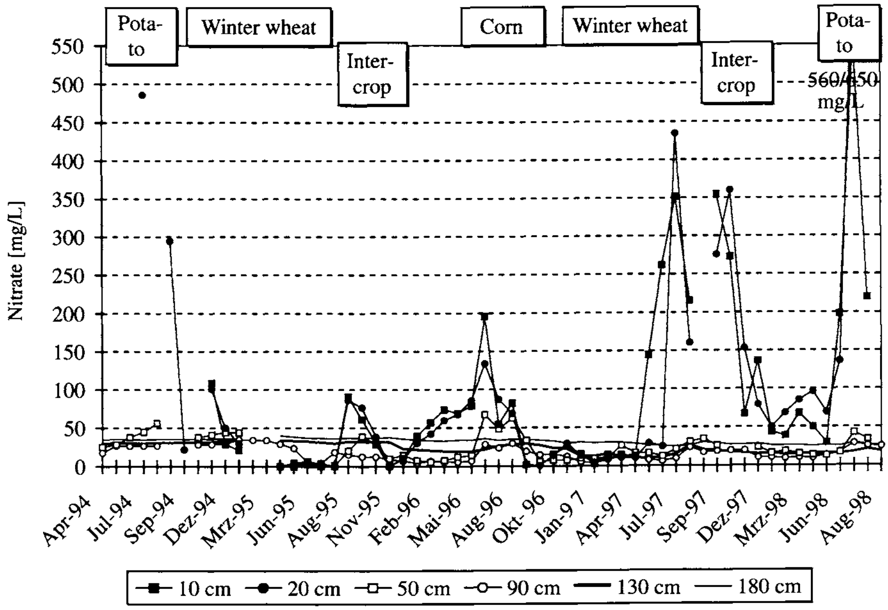

Figure III.3.11. The variation of nitrate concentrations in a soil profile of Scheyern (Upper Bavaria); nitrate peaks are the response to fertilizing (Hellmeier, 2001).

Considering the transport of DOC, nitrate and sulfate from the hilly area, Hellmeier (2001) stated (see Chapter V.2.2, Figure V.2.2.8) that, in general, the export of sulfate and chloride through surface run-off, interflow and groundwater recharge was of the same order of magnitude as determined by the analysis of discharge in creeks. DOC colloids were predominantly exported by the interflow, because within the effective root zone the mechanical filtration of particles was less pronounced as compared to the sediment beneath. Chloride and sulfate occur as dissolved, and DOC as suspended matter in the discharge components.

In the presence of chlorides and sulfates on one hand and DOC on the other hand, nitrates behave intermediately (see Chapter V.2.2, Figure V.2.2.8). Obviously nitrates are not only exported as a dissolved matter, but probably also as a DOC-bound matter.

III.3.4. Concluding remarks

Pesticides and fertilizers seriously affect ground and surface water quality if not adequately applied. Since one important pathway in agriculture areas is linked to discharges (overland runoff, inter-flow and groundwater-recharge) transporting agrochemicals as solute or particle-bound matter, the application should be much more oriented on weather conditions and the soil in-homogeneities; rainy seasons mostly favor the export of agrochemicals as compared to the end of rain events or long before the rainy season. Repeated application of small amounts of agrochemicals according to the needs of plants is preferable, as it would allow to adjust the agrochemical addition to the uptake by the crop and thus to reduce their losses.

The oxidation status of inorganic agrochemicals has a considerable influence on their export potential through discharge. It is potentially the highest in seasons without crops when significant soil aeration occurs, and the lowest in the vegetation period due to the reducing chemical environment and the storage function of the effective root zone. Both these factors that affect the mobility of agrochemicals can be regulated to the significant extent by seeding intercrops and by applying fertilizers according to plant needs and soil retention capacities. Pesticides also should be applied in much smaller quantities than usual and better repeatedly. Much more research is needed to elucidate the metabolisms as well as toxic effect and mobility of these substances. The routine pesticide tests do not satisfy the water protection requirements.

Also the kind of soil treatment and the crops itself contribute significantly to the transport of agrochemicals to surrounding compartments, resulting in hazardous concentrations in the aquatic environment and soils.

Taking into account the variety of factors influencing the mobility of agrochemicals, precision in farming probably could contribute much more to adequate environmentally friendly agricultural activities than usual ecological or intensive farming.

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