The land surface is exposed to different contaminant sources (air, household, dump sites, industry, traffic and agriculture). Contamination may reach subsurface waters enhanced by special surface receptors (e.g. interception evaporation) and become transported by overland flow, interflow and infiltration (Sect.1.4) to surface and groundwater.

The emission of contaminants is partly produced by combustion processes, introducing $\text{H}_2\text{O}^+$, $\text{NO}_x$, $\text{SO}_x$, $\text{CO}_2$, heavy metals and organics into the atmosphere. They subsequently reach the land cover either by interception (dry and wet) or directly by precipitation (wash out). Usually the contaminant concentration in interception deposition and in air are equal. The former may even be larger because of evaporation at the interceptor surfaces (tree leaves). In rainy deposition, on the contrary, the contaminant content is mostly diluted.

A contaminants in the air have been accumulated over a long period of time and can not be regulated, that is, at this scale there is no possibility to clean the atmosphere by technical means on a short term. Their presence is most prominent close to the emitting source, and in forest areas, especially at the regional air moisture condensation level where moisture condensation may contribute as much to precipitation as rain itself. The pollution is usually higher in air moisture than in precipitation, so that the pollution deposition is much stronger than by rain alone. The deposition is lowest on bare soils.

Another contamination source for land surfaces is the excessive distribution of agrochemicals (organic and inorganic), used to support and enhance soil fertility and to protect plants. Its impact on subsurface resources can to some extend be governed as far as the application is not too excessive and the time of application with respect to meteorological conditions is carefully selected.

Groundwater is not completely exposed to all contaminants, as some of them become sorbed on soils or are being exported in dissolved condition or particle bound by interflow (Sect.1.3). In the unsaturated zone the contaminants may undergo chemical or microbial disintegration as far as the habitat and flow conditions favor microbial activities.

Artificial tracer and natural isotope methods may be applied to trace the history of elements, to recognize the efficiency of chemical or microbial environments like biofilms, and time spans for disintegration processes. They can also contribute to developing long-term strategies of groundwater protection (Seiler et al. 1992). In this respect an interesting field of applications are the biporous media to which belong most of the Mesozoic hard rocks.
explored for groundwater abstraction. Such media offer simultaneously high storage, considerable dilution and efficient drainage capacities.

5.1 THE ROLE OF SEDIMENT FACIES IN STORAGE AND DISINTEGRATION OF AGROCHEMICALS IN THE KARST OF SOUTH GERMANY

5.1.1 INTRODUCTION

Bedrock aquifers are commonly highly heterogeneous. The frequency distribution of individual flow velocities in these aquifers covers a wide and discontinuous range, so creating storage and drainage conditions for seepage and groundwater flow. However, this cannot be recognised from average hydraulic parameters obtained by traditional methods, which may lead to problems in assessing natural attenuation processes, groundwater exploration and short- and long-term aspects of groundwater protection.

Hydraulic tests are based on pressure equilibration as well as on mass transport. Tracer tests, on the contrary, provide information exclusively about mass transport, which is a particularly important consideration for the above-mentioned processes.

![General stratigraphic section of the carbonates of the Franconian Alb, starting from the Dogger/Malm interface (Meyer & Schmidt-Kaler 1989).](image)

Fig. 5.1 General stratigraphic section of the carbonates of the Franconian Alb, starting from the Dogger/Malm interface (Meyer & Schmidt-Kaler 1989).
5.1.2 THE MALM CARBONATES OF THE FRANCONIAN ALB

The carbonates of the Franconian Alb, Germany, belong to two consecutive cycles of sedimentation, each of which starts with a marl facies and changes gradually into bedded limestones. In the upper cycle, however, reefs replace bedded limestones over significant stratigraphic intervals (Fig.5.1).

Bedded limestones typically lack syngenetic porosity, but are characterised by narrow or open fissures and solution channels. Unlike the bedded limestones, the reef dolomites commonly have porosities (Weiss 1987)

- of sedimentary and early diagenetic age,
- due to weathering of dolomites,
- from fissures and
- solution processes.

These porosities of different origins in the reef facies lead to a broader spectrum of individual hydraulic conductivities than in the bedded facies. As a result, flow velocities in the reef facies range from a few meters per year to kilometres per day, whereas velocities in the bedded facies range from few hundred meters to kilometres per day.

5.1.3 RESULTS OF TRACER EXPERIMENTS

The research area covers about 1000 km² within the Upper Jurassic. More than 150 tracer tests have been executed with fluorescent dyes that behave conservatively with respect to flow velocities (Behrens 1971).

About half of the tracer tests (Fig.5.2) have been performed in the bedded facies: tracer recovery and flow velocities were mostly high. During an observation time of more than 7 years, tracer tests in the reef facies ended as a rule at distances exceeding 1.5 to 2 km without recovery.

Statistical evaluation of measured flow velocities leads to the following classification:

- group I  610 ± 330 m/d
- group II  2135 ± 533 m/d
- group III  4190 ± 925 m/d.

Flow velocities of group I result in an average hydraulic conductivity of about 5×10⁻³ m/s, which agrees well with results from pumping tests (Seiler et al. 1992). Flow velocities exceeding 1000 m/d likely reflect the existence of preferential flow path. On the other hand, low hydraulic conductivities that do not appear to be consistent with tracer experiments are also known from pumping tests. This could be attributed to a more pronounced dilution of tracers.
In one area the catchment is crossed by a steep, vertical boundary between the bedded and reef facies of non-tectonic origin (Fig. 5.3). All tracer tests in the bedded facies have been recovered. In the reef facies, however, recovery did not occur at distances in excess of 2 km. These must be attributed to a virtual retardation of the conservative tracer, due to diffusive and convective tracer exchanges between fissures and matrix porosity. A comparison of fissures in both areas revealed that high fissure intensities and low fissure apertures characterise the bedded facies. In contrast, fissuring in the reef facies is less intensive and fissures have larger openings (Seiler et al. 1992). Hydraulic conductivities in the reef facies should thus exceed those of the bedded facies, but flow velocities measured by tracer experiments are even lower in the reef than in the bedded facies. This again is linked to diffusive tracer exchanges between fissures and the porous matrix in the reef facies.

5.1.4 THE DILUTION OF DYE TRACERS

The concentration-time curves for tracer tests in the study area can be subdivided into three categories (Fig. 5.4):

1) high concentration maxima and narrow geometry (curve 1 in Fig. 5.4) point to high flow velocities (> 1.5 km/d) and low dispersivities; such results are attributed to flow in solution channels
Fig. 5.3 Results of tracer tests along a vertical, non-tectonic interface between bedded and reef facies. Tracer recovery was high in the bedded facies; in the reef facies no tracers were recovered.

2) lower concentration maxima than before mentioned and a less narrow geometry (curve 2 in Fig. 5.4) point to flow in fissures with some diffusive tracer exchange between large and narrow fissures

3) very low concentration or undetectable tracer maximum over 1.5 km (the detection limit of fluorescent dyes is 2 to 20 ng/L) and a pronounced tailing (curve 3 in Fig. 5.4) is produced by a diffusive and convective tracer exchange between the small volume of water in fissures (< 2 vol.%) and the huge volume of water in a low hydraulic conductivity matrix (3 to 20 vol.%).

Fig. 5.4 Concentration versus time curves from the Malm carbonates of the Franconian Alb. Results from tracer propagation in 1 = solution channels, 2 = fissures of the bedded facies; 3 = reef facies; note that for curve 3 the time scale is 100 times larger than in cases 1 and 2.
5.1.5 TRITIUM IN GROUNDWATERS FROM BEDDED AND REEF FACIES

Tracer tests provide sectorial information about groundwater flow. In contrast, environmental isotopes like $^3$H can be used to add aerial information on the groundwater flow field. During the dry season, for example, a clear difference exists in $^3$H concentrations of groundwaters from bedded and reef facies:

- in the bedded facies $^3$H concentrations are close to the mean of precipitation of the last few years (Seiler et al. 1995) (Fig. 5.5),
- in areas with less than 1% of tracer recovery $^3$H concentrations are significantly lower and stand for mean residence times exceeding 100 years (Fig. 5.6).

![Fig. 5.5 Water ages in the reef and bedded facies based on $^3$H data.](image)

Some springs have been sampled during 10 years, once a year at the end of the dry season. $^3$H evaluation of this sampling shows mean residence times exceeding 50 to 200 years (Fig. 5.6). This is based on an exponential age distribution, referring to dry weather discharge conditions. The high mean residence times do not mean that the artificial tracers in these springs could not be recovered. The results of the tracer experiments, however, point to very low recoveries over short distances as well as low flow velocities, both characteristic for fissured rocks with high matrix porosities.
5.1.6 FATE OF NITRATES IN THE REEF FACIES

The huge water storage capacity of the reef facies could lead to long-term problems in groundwater quality, as far as no biologic disintegration exists. In the research area nitrogen excess amounts to 60 kg/ha per year, while the groundwater recharge is about 255 mm/a. From these numbers a concentration of 24 mg N/L or 100 mg NO₃/L is expected in the Karst groundwater. In the bedded facies the real concentrations indeed range from 60 to a maximum of 80 mg/L. In the reef facies, however, the values are below 20 mg/L (Fig.5.7). The aquifer without matrix porosity shows the current pollution situation, whereas the aquifer without is either not yet fully charged with pollutants, or the pollutant concentration is decreased by microbial processes in the rock matrix (Seiler 1997).

5.1.7 BACTERIAL POPULATIONS IN THE UNDERGROUND

Water samples of springs and wells from areas with different land use (agriculture: A1-A2, forestry: A3-A4) were analysed microbially. The rocks of these areas consist of reef. The total bacterial numbers (DAPI-stain) and colony forming units (cfu) were quantified on R₂A agar (aerobic incubation, 22°C) and on a denitrification agar (R₂A agar + 0,5% KNO₃, anaerobic incubation, 22°C). In addition, of some bacterial isolates the denitrifying activity was analysed.

Fig. 5.6 ³H concentrations in springs from the reef facies at the end of the yearly dry period.
Fig. 5.7  Average concentration of agrochemicals in groundwater from aquifers without (bedded facies) and with matrix porosity (reef rocks) in the Franconian Alb, Germany (Glaser 1998).

The groundwater samples from agricultural and forest areas had total bacterial counts of $2 \times 10^5$ to $9 \times 10^5$/mL and $5 \times 10^4$ to $1 \times 10^5$/mL, respectively. As compared to the total counts, only less than one percent could be cultivated on R2A agar. Colony forming units were 100 to 700/mL (A1, A2) and 30 to 200/mL (A3-A4). The cfu’s did not show significant seasonal differences from July to December. Under anaerobic conditions only 1 to 10% of the cfu’s were growing. The water samples of reef facies from the agricultural (A1-A2) or forest areas (A3-A4) have anaerobic cfu’s between 7 and 30/mL or between 1 and 4/mL, respectively. In the samples of the agricultural areas there are a higher numbers of total and viable counts as compared to those of the forest areas.

Some bacterial colonies, which were growing under anaerobic conditions, were isolated and analysed for denitrifying activity. The physiological tests showed that all of these bacteria reduce nitrate to nitrite, only some produce gas in an anaerobic atmosphere in nitrate containing media.
**Fig.5.8** Colony forming units (cfu) on denitrification agar (R2A agar + 0.5% KNO3) under anaerobic conditions.

### 5.1.8 LABORATORY DENITRIFICATION EXPERIMENTS

It is important not only to study microbial activity of cultivated bacteria, but also to analyse the denitrifying potential of groundwater in comparison with biofilms. Groundwater samples (300 mL) were incubated for 3 weeks under anaerobic conditions. 50 mg NO$_3^-$/L and no supplementary carbon source were added to the water samples. The DOC content of the groundwater samples of both areas was about 2 mg/L and the natural nitrate concentration of 9 to 12 mg NO$_3^-$/mL. The NO$_3^-$ and NO$_2^-$ concentrations in the water samples were measured during an anaerobic incubation (Fig.5.9 A and B). Clearly, a decrease in NO$_3^-$ and a concomitant increase in NO$_2^-$ were observed in the incubated water samples. In the water samples from the agricultural area NO$_3^-$ loss and NO$_2^-$ production started after 7 days. After 16 days a decrease of NO$_2^-$ was observed. This higher activity in NO$_3^-$ disintegration in samples A1 as compared to A3 could be explained by the higher anaerobic cfu's of sample A1 (Fig.5.8). In addition to the NO$_2^-$ production, the N$_2$O development was measured. In sterile controls no denitrifying activity was found. These results demonstrate, that the
Concentration changes of nitrate and nitrite in anaerobically incubated water samples from agriculture (a) and forest areas (b); 50 mg NO$_3^-$/L and no additional carbon source was added. This proposal with a and by here is accepted

groundwaters of two of the Karst areas exhibit a substantial denitrifying activity, despite of very low organic carbon supply. It is hypothesised, that some autotrophic activity exists in these water samples that are very rich in dissolved carbonate (370-390 HCO$_3^-$ mg/L). Since most of the micro-organisms, living in a kind of quick sorption and slow desorption equilibrium, are settled on surfaces, sterilised rock pieces were inserted in wells and springs to harvest micro-organisms in biofilms at the rock surface. The same denitrification test as shown in Fig.5.8 has been executed with biofilm micro-organisms. As a result, from all tests this denitrification process was much faster.
Since denitrification needs anaerobic conditions, while the redox potential of groundwater is in the range of +400 mV, it was supposed that the denitrification process is focused on biofilms. If so, in this reducing environment an isotope shift in $^{34}\text{S}$ or $^{15}\text{N}$ was expected, leading to respective isotope enrichment in the low energetic phase (Fig. 5.10). First results indeed demonstrate that in groundwater these isotope concentrations increase. This is not as spectacular as it primarily was in biofilms, because the isotope concentrations decrease after release from biofilms.

![Figure 5.10](https://example.com/fig510.png)

**Fig. 5.10** $^{34}\text{S}$ and $^{18}\text{O}$ concentrations in groundwaters with high redox potential (+400 mV).