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# Biodegradation: Updating the concepts of control for microbial clean-up in contaminated aquifers

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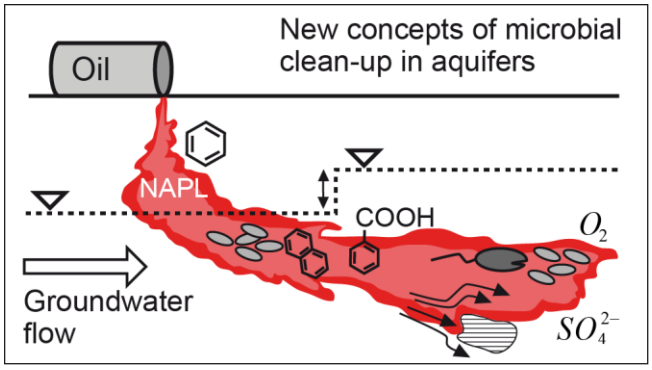
# Biodegradation: Updating the concepts of control for microbial clean-up in contaminated aquifers

**Authors?**

## Abstract

Biodegradation is one of the most favored and sustainable means of removing organic pollutants from contaminated aquifers but the major steering factors are still surprisingly poorly understood. Growing evidence questions some of the established concepts for control of biodegradation. Here, we critically discuss classical concepts such as the thermodynamic redox zonation, or the use of steady state transport scenarios for assessing biodegradation rates. Furthermore, we discuss if absence of specific degrader populations can explain poor biodegradation. We propose updated perspectives on the controls of biodegradation in contaminant plumes. These include the plume fringe concept, transport limitations, and transient conditions as currently underestimated processes affecting biodegradation.

## Abstract Art




## 1. Introduction

Over the last 150 years, the number of organic chemicals released into the environment has increased dramatically [1], leaving an unprecedented chemical footprint on earth. Many groundwater contaminations result from point sources, originating from accidents or contaminations at industrial

sites. These contaminations typically form plumes with high concentrations of pollutants (µg/L to mg/L range). Alternatively, chemicals may enter groundwater via widespread application in agriculture or release from sewage treatment into rivers. Here, pesticides, pharmaceuticals, or consumer care products are introduced as non-point sources and typically occur in much smaller concentrations (micropollutants in ng/L to µg/L range) [2].

For what seems at first sight a daunting perspective, nature fortunately has a remedy in place: biodegradation. Microorganisms can oxidize organic pollutants to $CO_2$ while reducing electron acceptors such as molecular oxygen, nitrate, Fe(III) (and other metal oxides), or sulfate (Fig. 1). Alternatively, some pollutants such as chlorinated solvents may serve as electron acceptors (Fig. 1, right side).

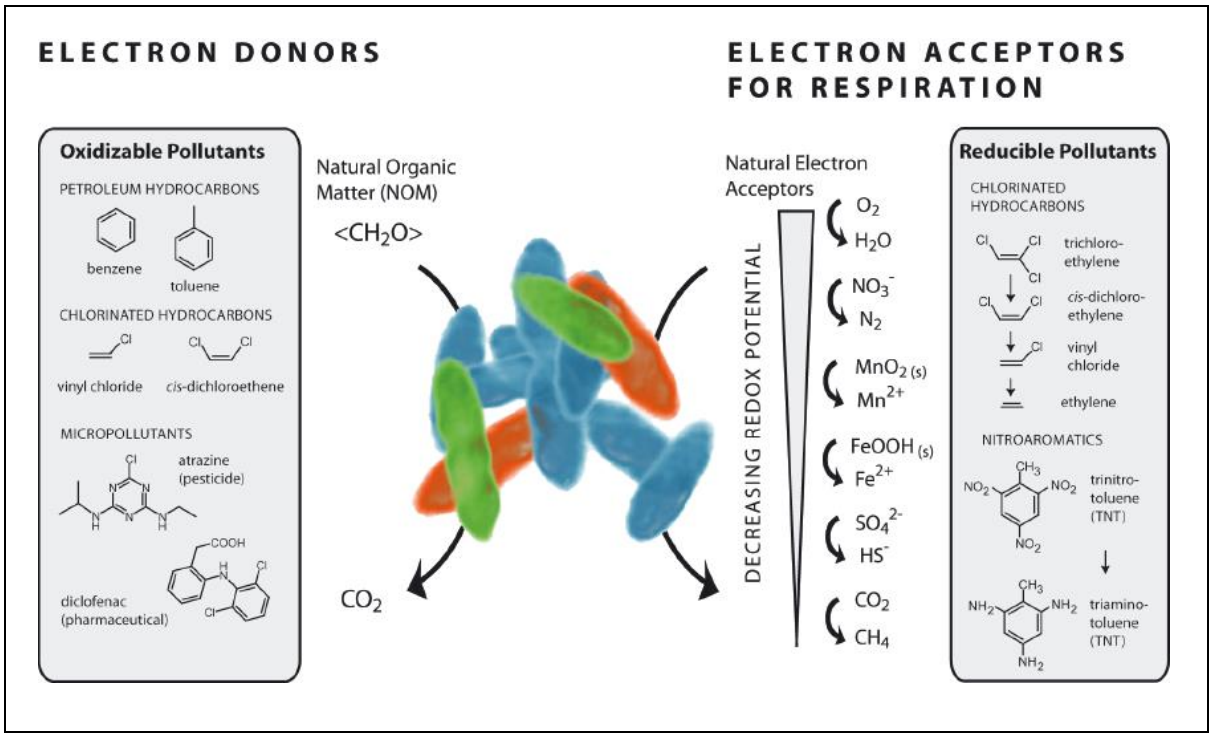



**Fig. 1.** Contaminants can serve as electron donors or acceptors for aquifer micro-organisms.

However, despite decades of biodegradation research, the true drivers governing contaminant degradation are still poorly understood. This article revisits and challenges current concepts on the controls and limitations of biodegradation in aquifers. It critically discusses (i) whether biodegradation is primarily governed by thermodynamics (i.e., redox zonation) at contaminated sites, (ii) if biodegradation can be adequately predicted by considering the subsurface as one reactive compartment and applying terms of environmental engineering (residence time, reaction

time), and (iii) the biological controls of biodegradation. We argue that groundwater ecosystems are much more heterogeneous and dynamic than currently perceived. Furthermore, we suggest that kinetic controls of biodegradation have been largely overlooked. Current concepts rely to a large part on thermodynamic considerations and steady state assumptions, while processes are frequently dynamic. In many cases, the steering parameters were not considered at appropriate spatial and temporal scales. However, the crucial controls of biodegradation discussed below provide potential for changing the future design of scientific projects, monitoring campaigns, or remediation strategies.

## 2. Revisiting redox zonation in contaminated aquifers

In highly polluted aquifers (e.g. petroleum spills with hydrocarbon concentrations of up to 100 mg/L), an excess of dissolved electron donors (hydrocarbons) prevails over acceptors (Fig. 1). In such contaminant plumes, electron acceptors are readily depleted which is widely accepted as a major limitation of biodegradation [3, 4]. A longitudinal sequence of redox processes is assumed: methanogenic degradation close to the contaminant source, followed by sulfate reduction, manganese(IV) and iron(III)-oxide reduction, nitrate reduction, and finally aerobic processes towards the distal end of the plume [3-7] (Fig. 2 A). However, this redox zonation concept is challenged in the following.

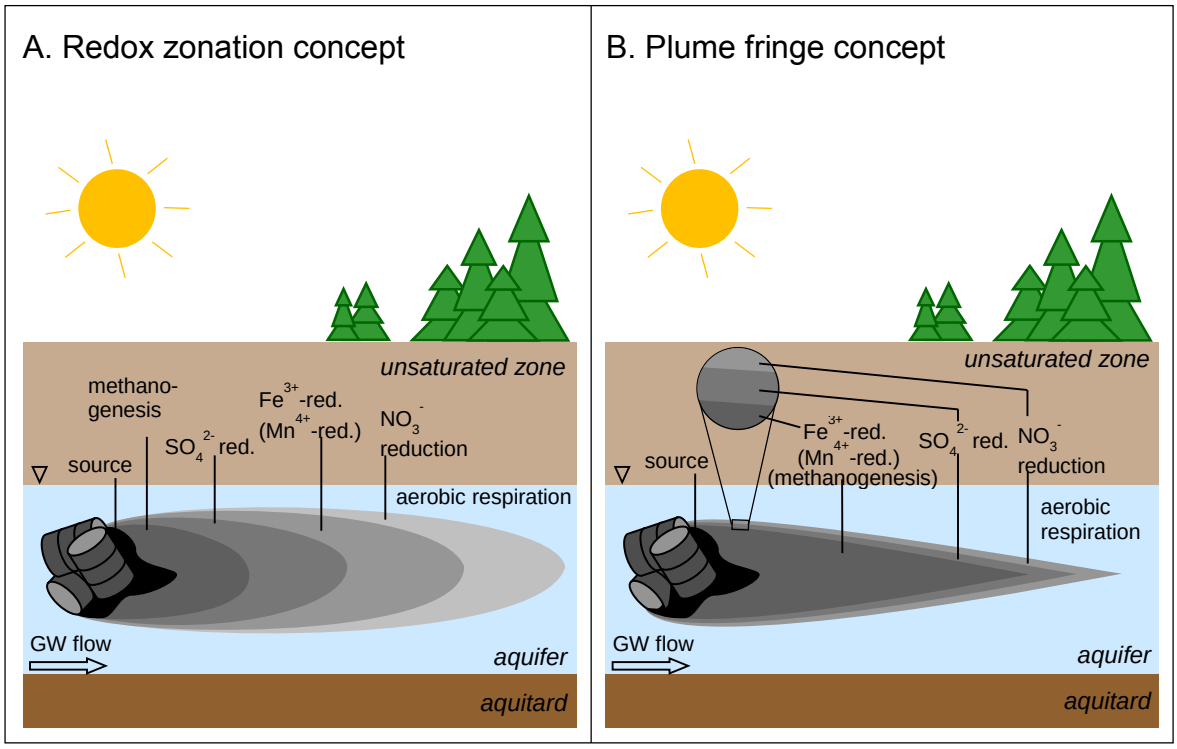


**Fig. 2.** Comparison of the longitudinal redox zonation concept (A) and the plume fringe concept (B), both describing the spatial distribution of electron acceptors and respiration processes in a hydrocarbon contaminant plume. (B) Iron(III) reduction, manganese(IV) reduction, and methanogenesis may occur simultaneously in the core of the contaminant plume.

Dissolved electron acceptors depleted at the source zone cannot be readily replenished in the downstream plume due to laminar flow and the limited transversal dispersion in porous media (Fig. 2 B). Accordingly, methanogenic degradation or reduction of insoluble iron(III) and manganese (IV) phases would be the only electron-accepting processes possible in the source zone or the downstream plume core. Recent field evidence supports this theoretical concept showing electron acceptor depletion in the plume center [8,9]. This is an evident contradiction to the classical concept of reverse longitudinal redox zonation (Fig. 2A). If dissolved electron acceptors such as sulfate or nitrate are consumed already at the source, they cannot become available again downstream allowing for sulfate or nitrate reduction. Even if not all electron acceptors are depleted during the passage through the source zone, a downstream redox succession should develop, where first nitrate and sulfate reduction take place, followed by methanogenesis, and not *vice versa*. Such spatial distributions have indeed been found along contaminant plumes when sampling was performed at appropriate resolution [10,11].

### 2.1. Is thermodynamics alone determining microbial competition in contaminant plumes?

The theory behind every redox zonation model is that microorganisms reducing a thermodynamically more favorable electron acceptor can gain more energy (Fig. 1), e.g. nitrate- vs. sulfate-reducing bacteria[12]. In electron donor-limited systems such as aquifers with only little contamination, nitrate reducers should therefore be able to consume organic substrates to threshold concentrations no longer permissive for the activity of thermodynamically less favored respiratory guilds, which consequently become outcompeted [13]. However, in highly contaminated aquifers, electron donors are present in excess over the oxidation capacity of all electron acceptors and at concentrations much higher than where competition for electron donors (i.e., available organic substrate) can occur. Consequently, respiration processes should rather occur simultaneously as long as respective electron acceptors are present and do not become limiting for a certain respiratory guild. Biodegradation activity thus becomes controlled by availability of specific electron acceptors, rather than by thermodynamics. This concept is supported by studies on

electron acceptor-limited chemostats where axenic cultures express all respiratory pathways simultaneously rather than only the energetically most favorable [14-17].

We propose that the reason why more favored respiratory guilds may nevertheless appear in higher abundance is a kinetic advantage which is based on higher energy conservation. Conserving more energy leads to higher growth yields ($Y$) and, therefore, growth rates ($\mu$) (Equations 1-3; where $X$ is the total biomass, $X_0$ the initial biomass, $S$ the substrate concentration, and $t$ the time of observation).

$$\mu = \mathrm{d}X \div \mathrm{d}t \times 1 \div X_0 \quad (1)$$

$$\mathrm{d}X \div \mathrm{d}t = -Y \times \mathrm{d}S \div \mathrm{d}t \quad (2)$$

$$\mu = -Y \times \mathrm{d}S \div \mathrm{d}t \times 1 \div X_0 \quad (3)$$

Thus, nitrate reducers can grow faster and to higher cell numbers in a given plume compartment suggesting an apparent out-competing of inferior respiratory guilds by thermodynamics. We propose that in many cases this will be controlled by the availability of electron acceptors and not by thermodynamic competition between respiratory guilds. Recently, Hansel et al. reported that microbial sulfate reduction was dominant over iron-reduction in sediments despite the lower thermodynamic energy gain [18]. The study exemplifies the importance of bioavailability rather than merely the thermodynamic redox potential of the electron acceptor.

### 2.2. Importance of processes at plume fringes

In recent years, it became apparent that biodegradation in contaminant plumes is much better explained by the 'plume fringe concept' than by the classical longitudinal redox zonation (Fig. 2) [19]. This concept is founded on the depletion of dissolved electron acceptors in the plume core. Biodegradation with oxygen, nitrate, or sulfate reduction can then only take place at the fringes of the plume, where electron acceptors are replenished from surrounding groundwater by dispersion and diffusion ("mixing in") (Fig. 2 B) [8,19-21]. At an adequately high resolution of sampling, steep geochemical counter-gradients of electron donors and acceptors have indeed been observed in several contaminated aquifers thus verifying the 'plume fringe concept' [22-24]. The concept also provides an appropriate explanation for the overall rather limited net biodegradation rates in hydrocarbon plumes: the small-scale dispersive mixing at plume fringes controls the mass transfer of electron acceptors and, thus, microbial activities. On the other hand, the concept predicts that the plume fringes are the true hot spots where biodegradation occurs *in situ* [25,26].

The incomplete conceptual understanding of plume redox zonation brings about two fundamental caveats in many field investigations: (i) sampling at inappropriate scales and (ii) taking samples at the wrong spot [27,28]. Thus, many studies may actually have overlooked the most relevant processes and zones of biodegradation simply because groundwater sampling was done at meter rather than at centimeter resolution. While numerous studies reported on marked differences in overall microbial community assembly along plumes[29-32], vertical heterogeneity of biodegradation activities has rarely been considered [9,33,34]. Consequently, appropriately high resolution monitoring and the limitations of dispersive mixing still await a better incorporation into conceptual models and study design. Future research should investigate the generic conditions affecting the processes at the plume fringes and the limitations of biodegradation.

### 2.3. The plume core as a poorly understood compartment

Even when all dissolved electron acceptors are depleted, methanogenesis and Fe(III)- or Mn(IV)-reduction may still drive biodegradation of hydrocarbons in the plume core (Fig. 2 B) [35]. Evidence for iron-reduction has indeed been reported for contaminated aquifers [36-38]. Very little studies, however, exist on methanogenic hydrocarbon degradation in laboratory incubations which is probably due to the extremely slow growth of such cultures [39]. Even less documented is methanogenic hydrocarbon degradation in aquifers [10,11]. Methanogenic hydrocarbon degradation may thus seem limited in spatial extent or relative contribution to the overall biodegradation [40,41]. An explanation might be provided by a study where agitation has been shown to impede methane production in soil slurries [42], most likely by disturbing close spatial interactions between syntrophic fermenters and methanogens. By analogy, groundwater flow may also interfere with efficient interspecies electron transfer in methanogenic plume zones by flushing away hydrogen or acetate and thus interfering with the energy fluxes needed for methanogenic activity [43,44]. Nevertheless, the true extent of methanogenic processes in contaminated aquifers requires further elucidation.

## 3. Bottlenecks of degradation by mass transfer

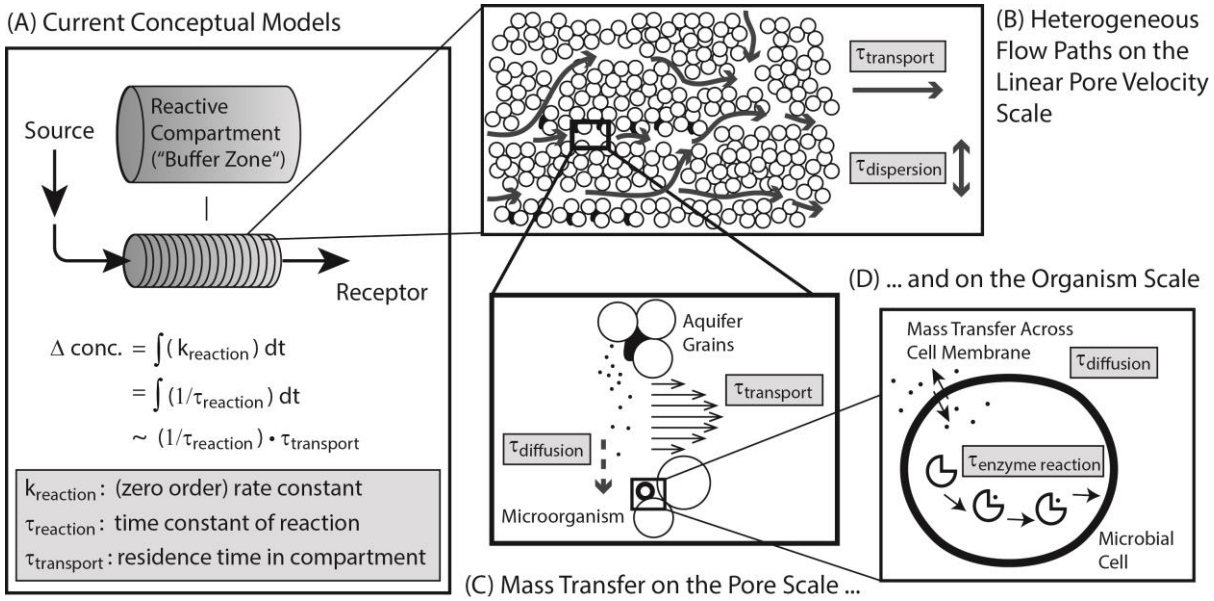



**Fig. 3.** Plug reactor or piston flow conceptual model of contaminated aquifers where contaminant removal (time constant of reaction, $\tau_{reaction}$) is inversely proportional to the average residence time $\tau_{transport}$ (A). However, the distribution of flow paths on the linear pore velocity scale (B), mass transfer on the pore scale (C), mass transfer through cell membranes on the organism scale, and (bio)chemical enzymatic transformation on the molecular scale (D) can be important bottlenecks of biodegradation not taken into account by the simplified model.

### 3.1. Average residence times ignore heterogeneous flow paths and flow velocities

Current conceptual models frequently treat natural sediments and aquifers like either completely mixed or plug flow reactors (Fig. 3A) [45,46]. In these models adopted from chemical engineering, a decrease in substrate concentration ($\Delta$ conc.) is proportional to the residence time ($\tau_{transport}$) in the reactive compartment (Fig. 3A). The relation of transport and degradation is frequently estimated from the dimensionless Damköhler number Da

$$Da = \frac{\tau_{transport}}{\tau_{reaction}} = \frac{\text{reaction rate}}{\text{transport rate}} \qquad (4)$$

where $\tau_{transport}$ is the mean residence time ("how long does it take for a compound to pass the compartment?") and $\tau_{reaction}$ the time constant of the reaction ("how long does it take for the compound to react?"). Note that the time constants are inversely correlated to the respective rates (Fig. 3A and Equation 4). The larger Da, the more biodegradation can potentially take place. This well-established concept might be a good proxy for identifying mass transfer as limiting factor in steady state systems dominated by advection. However, it is challenged by the fact that $\tau_{transport}$ and

$\tau_{reaction}$ are not well defined in natural systems because they depend on multiple parameters on different scales (Fig. 3). Black box approaches not considering multiple limitations will miss the opportunity for profound understanding of the steering parameters of such systems.

If transport is limiting on the pore velocity scale, increased flow velocities (decreasing residence times) may affect $\tau_{reaction}$ and increase biodegradation. This counterintuitive observation can be explained when considering that increased flow velocities induce more heterogeneous flow due to a wider distribution of flow paths length. This results in higher transversal and longitudinal dispersion [47,48] and thus increases the apparent reaction rate by bringing reactants together. However, also the opposite can occur and contaminants may bypass reactive zones due to increased preferential flow. Furthermore, changes in flow velocities can create unfavorable growth conditions [48] due to shifts in nutrient fluxes and redox conditions (see section 4) adversely affecting degradation (longer $\tau_{reaction}$). Concluding, the average residence time alone will not provide information on such ecological consequences. Rather, the distribution of residence times and the biogeochemical history along individual flow paths are governing mass transfer limitations in aquifers. This can be analyzed by high resolution monitoring which also allows for identifying dynamic flow fields and true solute fluxes [49]. However, there is a need to systematically investigate the influence of flow velocities and dynamic conditions on microbial degradation.

### 3.2. Does diffusion limit bioavailability on the pore scale?

In groundwater, most microorganisms are attached to sediments [50] where diffusion may become the dominant mode of substrate transport to cells at the pore scale [51,52] (Fig. 3C). If supply by diffusion is slow, biodegradation is availability-limited because microorganisms consume the substrate faster than it can be delivered [53]. The apparent $\tau_{reaction}$ in a given environmental compartment is then determined by $\tau_{diffusion}$ (Fig. 3C). Because diffusion to the cells takes place on the micrometer scale, steep diffusive gradients can create a situation in which much larger concentrations are observed in the surrounding water. Such limitations tend to be overlooked in conventional sampling. Whether or not such diffusion limitation is important, depends also on flow velocities because diffusion gets more important if water flow velocities are low [54]. This is exemplified in three scenarios regarding concentrations and the state of the system.

(i) At *high concentrations and steady state,* diffusive gradients between pore centers and sediment surfaces only build up if water flow velocities are low and if degradation rates are faster than the supply of contaminants. (ii) For *low concentrations and transient conditions* Langner *et al*. found that degradation rates of 2,4-dichlorphenoxyacetic acid were higher when water flow was slower, even

206 though the flow path was shorter [55]. This indicates that molecules needed sufficient time to diffuse
207 into micropores and $\tau_{transport}$ has to be sufficiently long compared to $\tau_{diffusion}$, since otherwise
208 molecules were flushed through the pores without degradation. (iii) For *low to medium*
209 *concentrations and at steady state,* one can expect that diffusive gradients become shallow if $\tau_{transport}$
210 is long and concentrations are low. Consequently, also the substrate supply by diffusive fluxes
211 becomes slower according to Fick's law. Then, higher flow velocities would actually be advantageous
212 because they replenish the substrate creating steeper gradients and increasing diffusive substrate
213 supply to the organisms.
214 Thus, the pore water velocity is an important parameter contributing to diffusion limitations on the
215 pore scale. However, both, too high and too small pore water velocities can induce limitations in
216 bioavailability [51] which implies a need for a systematic elucidation of this topic.

217 **3.3. Thermodynamics, mass transfer, or enzyme kinetics: what is limiting on the organism scale?**

218 It is often observed that micropollutants are only incompletely degraded even when competent
219 bacterial degraders are present[56]. This unsolved paradox of threshold concentrations might be due to
220 different reasons. (i) Thermodynamic limitation for biodegradation is an often considered explanation,
221 but can typically be excluded. For example at nM toluene concentrations, the Gibbs enthalpy of
222 reaction $\Delta G$ for aerobic degradation (-3890 kJ/mol) would be large enough to consume even the last
223 toluene molecule. At high dilution, biodegradation is rather kinetically limited by mass transfer to the
224 cell as explained above. (ii) An alternative explanation for incomplete degradation is a kinetic
225 limitation by insufficient substrate uptake into the cell[57]. (iii) Furthermore, slow biochemical
226 transformation rates (enzyme kinetics) might be due to the intrinsically difficult-to-degrade molecular
227 structures of xenobiotics[58]. This is supported by comparably slow degradation rates of persistent
228 compounds at higher but non-toxic concentrations in batch cultures[59].

229 In natural systems, it was so far not possible to distinguish the different kinds of limitation of
230 biodegradation on the organism scale, which opens future research fields.

231 **4. Microbial controls of biodegradation**

232 Absence of specific degrader populations is often assumed when insufficient biodegradation is
233 observed at a given site. At organohalide-contaminated sites, bioaugmentation (amending
234 respective degraders) of microbial consortia containing e.g. *Dehalococcoides* (Dhc) strains capable of
235 reductive dechlorination of trichloroethylene (TCE ) to ethene has been successful [60-62]. Similarly, the
236 effectiveness of bioaugmentation in atrazine- and MTBE-contaminated (methyl-tert-butylether)
237 aquifers has been demonstrated [63-65]. However, even highly specialized organohalide-respiring

bacteria are generally widespread in aquifers[66-68]. Thus for certain settings, it remains questionable whether respective degrader organisms were truly absent before bioaugmentation or only present at very low abundance.

**4.1. Limitation of biodegradation by microbial growth.**

In aquifers, a substantial fraction of the microbes is suggested to be in a status of low activity,inactive, or even dormant [69]. Moreover, microbial communities in aquatic systems exhibit growth efficiencies (yields) much lower than known from batch cultures and chemostats, with median values below 0.3 (g biomass / g substrate) for rivers, lakes, and oceans[70,71]. *In situ* growth rates are also low (equation 3) for aquifer systems, and doubling times can be in the range of months to years [72]. Under optimum conditions in the laboratory, the presence of one degrader cell at the moment of a hydrocarbon spill would allow aerobes to form notable biomass (e.g. $10^5$ to $10^6$ cells per liter groundwater) within a day, while e.g. sulfate reducers or organohalide reducers (doubling time: ~10 d) may require >100 d to establish a critical population size. Indeed, a fast response has been observed for an oxic aquifer system receiving a short contaminant pulse[73], while anaerobic degradation coupled to denitrification established only over several weeks. For more recalcitrant compounds and pollutants, requiring anoxic conditions for degradation (such as halogenated solvents), it might take years before reasonable numbers of degraders have developed. Thus in aquifers, a slow community response might be misinterpreted as absence of degrader populations which needs to be verified in the future.

**4.2. Limitations of biodegradation by microbial physiology**

Total concentrations of dissolved organic carbon (DOC) in pristine groundwater are usually in the low mg $L^{-1}$ range (0.5-2 mg $L^{-1}$), of which only 0.5 to 5% are readily assimilable organic carbon (AOC)[74-76]. This AOC consists of a plethora of individual compounds at extremely low individual concentrations, including organic micropollutants such as pesticides, pharmaceuticals, and many other low-level contaminants[77]. The latter are often present below the threshold concentrations of initial induction of catabolic genes and degradation pathways[75]. At very low concentrations in the environment, it is likely that microorganisms do not feed on only one substrate at a time. Mixed substrate utilization – where microbes can utilize a wide range of offered substrates simultaneously - has been observed in carbon-limited chemostats[78]. This leads to much lower threshold concentrations for individual compounds implying that the degradation of one compound “helps” to degrade another compound in energetic co-metabolism. However, at excess of substrate in hydrocarbon plumes, catabolite repression, competitive inhibition, or metabolic flux dilution might take place [79,80].

Today, it is totally unclear how microbial metabolism is regulated in the environment. Such knowledge will be useful for designing strategies for removing micropollutants from drinking water in engineered systems or improving the licensing practice of pesticides[77].

### 4.3. Limitations of ecosystem response

Low microbial growth rates imply that even under steady state conditions where organisms can develop without disturbance, long time spans are required to establish significant degrader biomass and thus biodegradation capacities. However in contaminated groundwater, conditions are not necessarily in steady state [81-83]. In fact, temporal hydraulic fluctuations may represent a major control of biodegradation in groundwater by repeatedly changing the environmental conditions encountered by degraders (e.g. sudden exposure of anaerobes to oxygen). This can be exemplified by plume fringes which are characterized not only as hot spots of biodegradation activity, but also by an apparently 'specialized' degrader microbiota [25,9] over only a few dm. If the prevailing geochemical conditions for microorganisms shift, degraders must continuously follow or re-establish in other strata. Geochemical shifts of the plume could thus represent a further, as-yet unrecognized kinetic limitation of biodegradation.

Moreover, transient supply of substrates by such fluctuations may not be sufficient to support growth of degrader populations. It can be speculated that under spatially and temporarily dynamic hydraulic conditions, degrader populations may never reach the biomass levels required to efficiently degrade substrate pulses. Once formed, however, degrader biomass may persist for months and perhaps even years after the source of contamination has disappeared [73,84]. Biomass established upon previous locations of the plume could sustain biodegradation capacities for future contaminations. Thus, aquifers could become preconditioned to efficiently degrade pollutants.

### 4.4. Further research needs.

The role of grazers (protozoa) and viruses (phages) in shaping prokaryotic degrader communities and influencing *in situ* degradation rates is totally overlooked to date [85]. While the influence of protozoa on bacterial community composition and *vice versa* has been shown also for contaminated groundwater habitats [86,87], there is contradicting evidence on either the stimulation [88,89] or inhibition [90,91] of biodegradation by protozoan grazing. Only a few studies are available on bacteriophages in groundwater [92-94] but their influence on degrader communities and activities have not been addressed, so far. Extrapolating recent advances from surface aquatic environments and marine systems, bacteriophages can be expected to play a significant role in controlling prokaryotic

production and diversity. With reference to the highly specialized degrader populations found in biodegradation hot spots, ecological concepts such as the 'killing the winner' hypothesis await to be tested. It predicts that when a given population grows beyond a critical density, grazers and viruses will decimate the population [95] affecting biodegradation.

## 5. Conclusion and outlook

Here we discuss several controls for biodegradation in contaminated aquifers that have been recognized in recent years, and call for an update of classical black box approaches in site assessment and restoration. New perspectives in groundwater research should include the plume fringe concept and mass transfer limitations as steering factors for biodegradation. On the organism scale, physiological properties of degraders and ecological drivers of degrader community structure have been identified to affect biodegradation. We propose that biodegradation in contaminated aquifers is largely controlled by kinetics. Different kinetic controls are interacting in complex ways and cannot be described by flow- or residence-time-dependent degradation rates alone. An important caveat is that many of these mechanisms act at the µm-to-cm scale, while sampling is still mostly conducted at the meter scale. To fully understand process limitations, samples have to be taken at adequate resolution, often including intact sediment cores or highly-resolved water sampling. Furthermore, temporal dynamics of processes demand for extended monitoring with more frequent sampling intervals in time and space.

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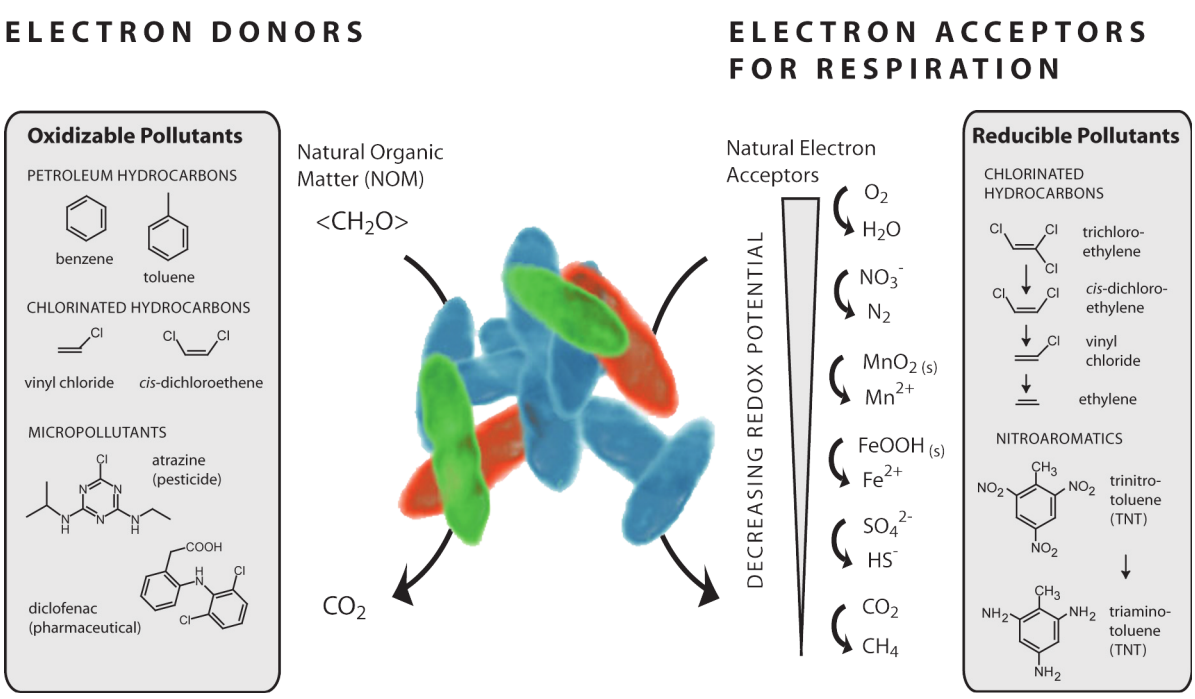
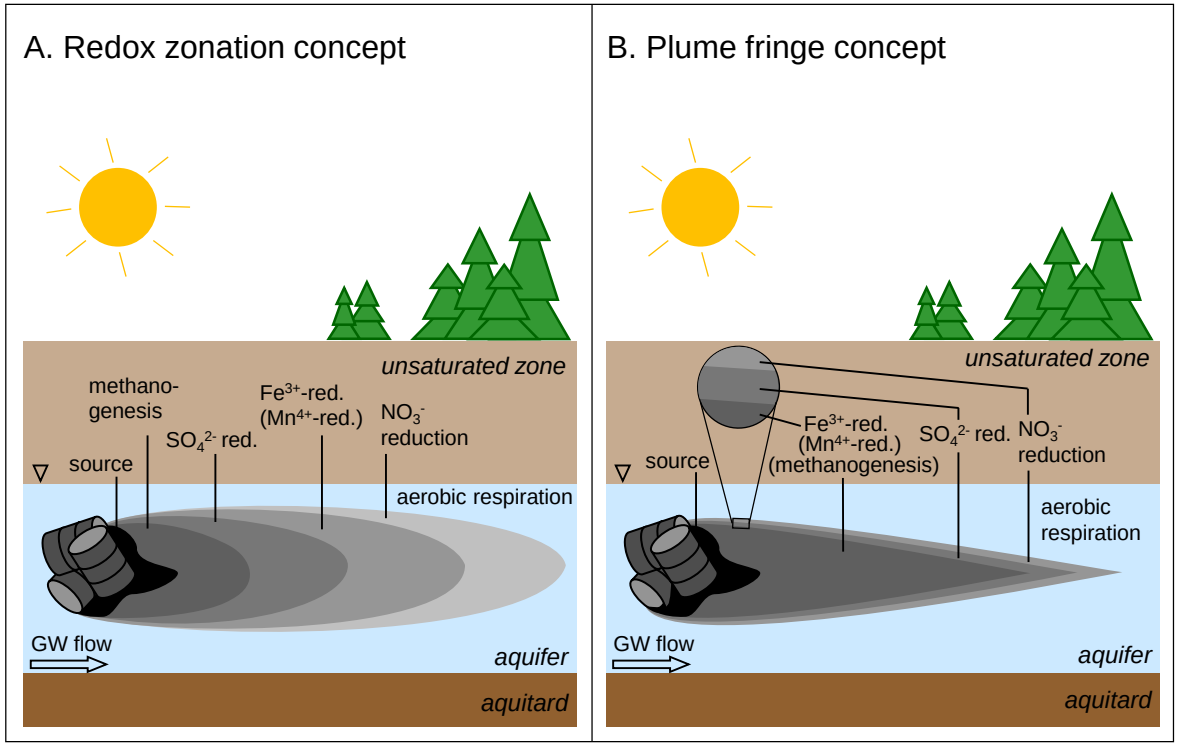
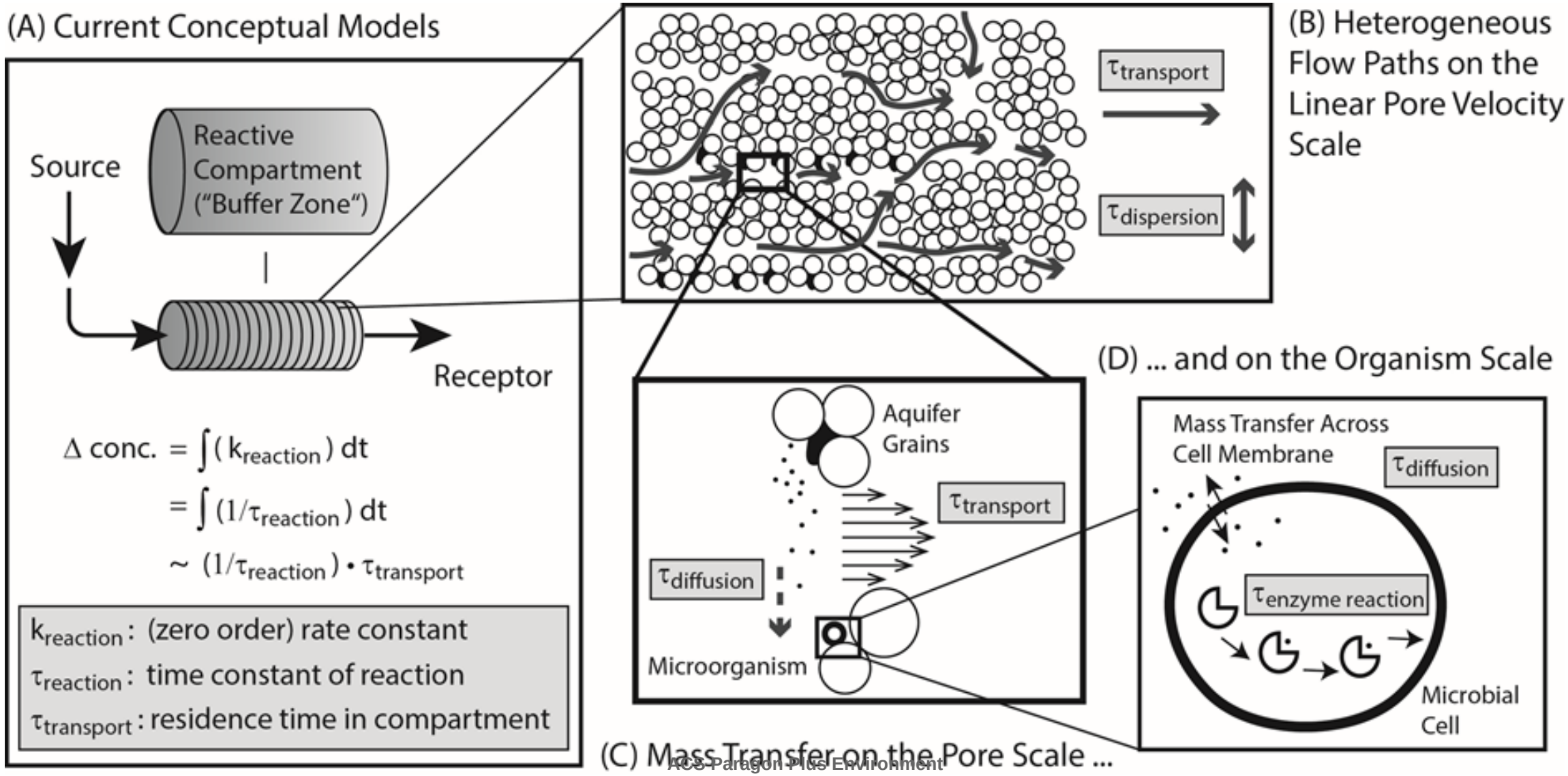
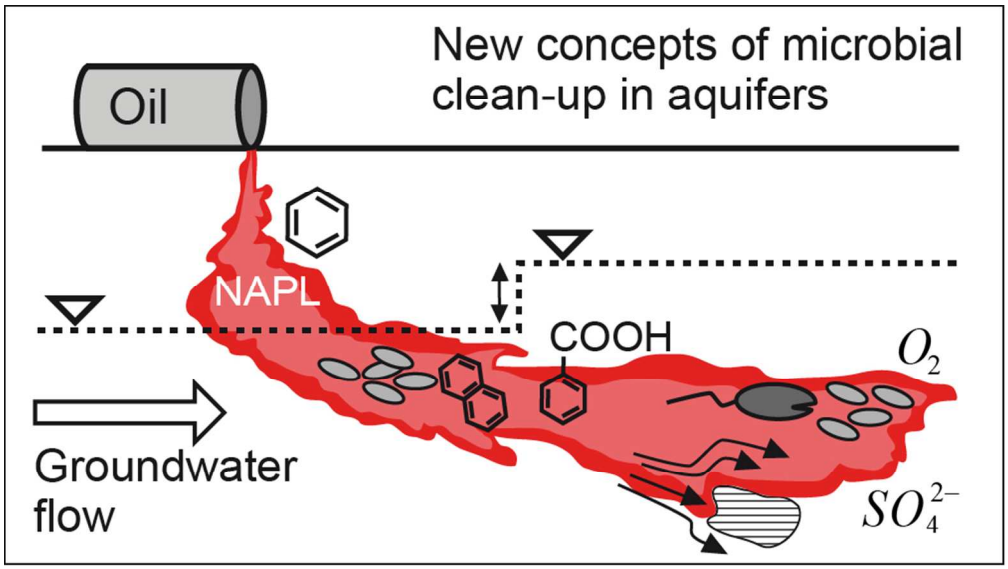

ELECTRON DONORS
ELECTRON ACCEPTORS FOR RESPIRATION
Oxidizable Pollutants
PETROLEUM HYDROCARBONS
benzene
toluene
CHLORINATED HYDROCARBONS
vinyl chloride
cis-dichloroethene
MICROPOLLUTANTS
atrazine (pesticide)
diclofenac (pharmaceutical)
Natural Organic Matter (NOM)
<CH2O>
CO2
Natural Electron Acceptors
DECREASING REDOX POTENTIAL
O2
H2O
NO3-
N2
MnO2 (s)
Mn2+
FeOOH (s)
Fe2+
SO4 2-
HS-
CO2
CH4
Reducible Pollutants
CHLORINATED HYDROCARBONS
trichloro-ethylene
cis-dichloro-ethylene
vinyl chloride
ethylene
NITROAROMATICS
trinitro-toluene (TNT)
triamino-toluene (TNT)


A. Redox zonation concept
unsaturated zone
methano-
genesis
Fe3+-red.
(Mn4+-red.)
NO3-
reduction
SO42- red.
source
aerobic respiration
GW flow
aquifer
aquitard
B. Plume fringe concept
unsaturated zone
Fe3+-red.
(Mn4+-red.)
(methanogenesis)
SO42- red.
NO3-
reduction
source
aerobic
respiration
GW flow
aquifer
aquitard


(A) Current Conceptual Models
Source
Reactive Compartment ("Buffer Zone")
Receptor
Δ conc. = ∫ ( k reaction ) dt
= ∫ (1/τ reaction ) dt
~ (1/τ reaction ) • τ transport
k reaction : (zero order) rate constant
τ reaction : time constant of reaction
τ transport : residence time in compartment
τ transport
τ dispersion
(B) Heterogeneous Flow Paths on the Linear Pore Velocity Scale
Aquifer Grains
τ transport
τ diffusion
Microorganism
(C) Mass Transfer on the Pore Scale ...
(D) ... and on the Organism Scale
Mass Transfer Across Cell Membrane
τ diffusion
τ enzyme reaction
Microbial Cell

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